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This document presents the results of a preliminary environmental assessment of the Chemically Active Fluid Bed (CAFB) process. All waste streams contributing air, water and solid waste pollutants were evaluated in terms of emission rates and potential environmental effects. As part of this investigation, a field sampling and laboratory analysis program was carried out to compile an emissions inventory of the CAFB pilot plant at the Esso Research Centre, Abingdon (ERCA), England. In addition to the environmental assessment, an economic evaluation of the CAFB relative to alternative residual oil utilization techniques is presented. Finally, recommendations are made for further control research and development to be carried out at the CAFB demonstration plant in San Benito, Texas.

CONTENTS

	Page
Abstract	iii
List of Figures	ix
List of Tables	xvi
Acknowledgments	xxi

Sections

		Page
I	Executive Summary	1
	Overview	1
	Conclusions	6
	References	10
II	Introduction	11
	The Chemically-Active Fluid Bed Process	11
	Program Objectives	12
	Report Organization	12
	References	15
III	Process Description	16
	Introduction	16
	Overview	16
	Fuel Feed System	27
	Limestone Handling System	28

CONTENTS (continued)

Sections		Page
	Gasifier	29
	Regenerator	33
	Spent Solids Handling System	36
	FW Resox^{TM} Off Gas Treatment System	36
	Boiler	37
	References	39
IV	Emissions Estimates	40
	Introduction	40
	Input Materials	41
	Fugitive Air Emissions From Oil Storage and Handling	46
	Fugitive Air Emissions From Resox^{TM} Coal Storage and Handling	48
	Fugitive Air Emissions From Limestone Storage and Handling	48
	Trace Element Emissions	50
	Water Emissions From Resox^{TM} Coal Storage	53
	Emissions From Resox^{TM} Solid Waste	55
	Emissions Associated With Spent Regenerator Stone	56
	Emissions and Environmental Effects of Condenser Cooling	57
	Emissions From Boiler Water Treatment and Boiler Blowdown	66
	References	69
V	Field Test Program and Laboratory Results	72
	Introduction	72
	Field Sampling Protocol	73

CONTENTS (continued)

Sections Page

Field Analysis 79

Laboratory Analyses 79

Field Test Program 90

Field Test Results 93

Laboratory Results 101

Summary 172

References 173

VI CAFB Air Quality Impact Assessment For The La Palma Retrofit 174

Introduction 174

Variables Affecting Ambient Concentrations 175

Dispersion Modeling Analysis 179

References 204

Appendixes

A Process Description and Emissions Estimates for the Coal-Fired CAFB 205

Process Description: 10 MW Demonstration Plant 205

Emissions Estimates: 10 MW Demonstration Plant 208

Process Description: 250 MW Coal-Fired CAFB 209

Emissions Estimates: 250 MW CAFB 214

References 220

B Comparison of the CAFB With Other Residual Oil Utilization Techniques 221

Introduction 221

Residual Desulfurization 222

CONTENTS (continued)

Appendixes		Page
	Environmental Impacts of Desulfurization Techniques	231
	References	235
C	Process Descriptions and Flow Diagrams of Residual Oil Desulfurization Techniques	236
	Flexicoking	236
	Gulf HDS	240
	RCD Isomax	243
	Residue Desulfurization (BP Process)	246
	Resid Hydroprocessing (Standard Oil Co. Indiana)	250
	LC-Fining	254
	Resid Ultrafining	255
	Go-Fining (Exxon Research and Engineering Co.)	259
	Residfining (Esso Research and Refining Company)	263
	Residue Hydrodesulfurization	265
	Hydrodesulfurization, Trickle	268
	IFP Resid and VGO Hydrodesulfurization	271
	Demetalization/Desulfurization	275
	Delayed Coking	276
	VGO/VRDS Isomax	279
	Shell Gasification Process	284
	References	289
D	Economics and Process Parameters of Alternative Residual Oil Utilization Technologies	291
	Introduction	291

CONTENTS (continued)

Appendixes | Page

Process Parameters of Feedstock Desulfurization 291

Economics of Feedstock Desulfurization Processes 291

Economic Comparison of FGD, HDS and CAFB 295

References 301

LIST OF FIGURES

No.		Page
1	Generalized Schematic of the CAFB	2
2	Unit Operations Flow Diagram of the ERCA Pilot Plant	18
3	Unit Operations Flow Diagram of the FW Demonstration Plant	20
4	Unit Operations Flow Diagram of the FW 250 MW Plant	23
5	Gasifier-Regenerator Schematic	30
6	Limestone Feed. Broadband ESCA Scan	45
7	Aerial Photograph of the La Palma Power Station	58
8	Fixed Bed Ion Exchange System	67
9	CAFB Pilot Plant	74
10	Pilot Plant Stack	75
11	Stack Sampling Ports	77
12	Adsorbent Sampling System	78
13	Hi-Vol Filter. Broadband ESCA Scan	85
14	Aluminum Substrate. Broadband ESCA Scan	
15	Vanadium Metal ESCA Scan	87
16	Vanadium Pentoxide ESCA Scan	88
17	Carbon 1s Binding Energies	89
18	Stack Particulate Size Distribution, Run No. 3. Fuel Oil Gasification	102
19	Stack Particulate Size Distribution, Run No. 5. Bitumen Gasification	103
20	Log-Normal Particulate Size Distributions	104
21	Bitumen, LC Fraction 1 IR Spectrum	108
22	Bitumen, LC Fraction 2 IR Spectrum	108

LIST OF FIGURES (continued)

No.		Page
23	Bitumen, LC Fraction 3 IR Spectrum	109
24	Bitumen, LC Fraction 4 IR Spectrum	109
25	Bitumen, LC Fraction 5 IR Spectrum	110
26	Bitumen, LC Fraction 6 IR Spectrum	110
27	Bitumen, LC Fraction 7 IR Spectrum	111
28	Bitumen, LC Fraction 8 IR Spectrum	111
29	Flue Gas From Bitumen Gasification, Run No. 7, LC Fraction 1 IR Spectrum	115
30	Flue Gas From Bitumen Gasification, Run No. 7, LC Fraction 3 IR Spectrum	115
31	Flue Gas From Bitumen Gasification, Run No. 7, LC Fraction 4 IR Spectrum	116
32	Flue Gas From Bitumen Gasification, Run No. 7, LC Fraction 5 IR Spectrum	116
33	Flue Gas From Bitumen Gasification, Run No. 7, LC Fraction 6 IR Spectrum	117
34	Flue Gas From Bitumen Gasification, Run No. 7, LC Fraction 8 IR Spectrum	117
35	Stack Cyclone Material From Bitumen Gasification, Run No. 5, LC Fraction 1 IR Spectrum	119
36	Stack Cyclone Material From Bitumen Gasification, Run No. 5, LC Fraction 2 IR Spectrum	119
37	Stack Cyclone Material From Bitumen Gasification, Run No. 5, LC Fraction 3 IR Spectrum	120
38	Stack Cyclone Material From Bitumen Gasification, Run No. 5, LC Fraction 4 IR Spectrum	121
39	Stack Cyclone Material From Bitumen Gasification, Run No. 5, LC Fraction 5 IR Spectrum	122

LIST OF FIGURES (continued)

No.		Page
40	Stack Cyclone Material From Bitumen Gasification, Run No. 5, LC Fraction 6. IR Spectrum	122
41	Stack Cyclone Material From Bitumen Gasification, Run No. 5. Broadband ESCA Scan	128
42	Stack Sampling Train Filter Material From Bitumen Gasification, Run No. 5. Broadband ESCA Scan	129
43	Stack Cyclone Material From Bitumen Gasification, Run No. 5. Vanadium ESCA Scan	132
44	Stack Sampling Train Filter Material From Bitumen Gasification, Run No. 5. Vanadium ESCA Scan	133
45	Stack Cyclone Material From Bitumen Gasification, Run No. 5. Sulfur ESCA Scan	135
46	Stack Sampling Train Filter Material From Bitumen Gasification, Run No. 5. Sulfur ESCA Scan	136
47	Regenerator Bed Material From Bitumen Gasification, Run No. 5, LC Fraction 1. IR Spectrum	138
48	Regenerator Bed Material From Bitumen Gasification, Run No. 5, LC Fraction 2. IR Spectrum	138
49	Regenerator Bed Material From Bitumen Gasification, Run No. 5, LC Fraction 3. IR Spectrum	139
50	Regenerator Bed Material From Bitumen Gasification, Run No. 5, LC Fraction 4. IR Spectrum	139
51	Regenerator Bed Material From Bitumen Gasification, Run No. 5, LC Fraction 5. IR Spectrum	140
52	Regenerator Bed Material From Bitumen Gasification, Run No. 5, LC Fraction 6. IR Spectrum	140
53	Regenerator Bed Material From Bitumen Gasification, Run No. 5, LC Fraction 7. IR Spectrum	141
54	Regenerator Bed Material From Bitumen Gasification, Run No. 5, LC Fraction 8. IR Spectrum	141

LIST OF FIGURES (continued)

No.		Page
55	Regenerator Bed Material From Bitumen Gasification, Run No. 5. Broadband ESCA Scan	143
56	Regenerator Bed Material From Bitumen Gasification, Run No. 5. Carbon ESCA Scan	145
57	Regenerator Bed Material From Bitumen Gasification, Run No. 5. Sulfur ESCA Scan	146
58	Stack Sampling Train Filter Catch During Bitumen Combustion and Fresh Limestone Feeding, Run No. 6. Broadband ESCA Scan	148
59	Stack Sampling Train Filter Catch During Bitumen Combustion and Fresh Limestone Feeding, Run No. 6. Carbon ESCA Scan	149
60	Stack Sampling Train Filter Catch During Bitumen Combustion and Fresh Limestone Feeding, Run No. 6. Sulfur ESCA Scan	150
61	Stack Cyclone Material From Fuel Oil Gasification, Run No. 4, LC Fraction 1. IR Spectrum	152
62	Stack Cyclone Material From Fuel Oil Gasification, Run No. 4, LC Fraction 2. IR Spectrum	152
63	Stack Cyclone Material From Fuel Oil Gasification, Run No. 4, LC Fraction 3. IR Spectrum	153
64	Stack Cyclone Material From Fuel Oil Gasification, Run No. 4, LC Fraction 4. IR Spectrum	153
65	Stack Cyclone Material From Fuel Oil Gasification, Run No. 4, LC Fraction 5. IR Spectrum	154
66	Stack Cyclone Material From Fuel Oil Gasification, Run No. 4, LC Fraction 6. IR Spectrum	154
67	Stack Cyclone Material From Fuel Oil Gasification, Run No. 4, LC Fraction 7. IR Spectrum	155
68	Stack Cyclone Material From Fuel Oil Gasification, Run No. 4, Broadband ESCA Scan	159
69	Stack Cyclone Material From Fuel Oil Gasification, Run No. 4, Vanadium ESCA Scan	160
70	Stack Cyclone Material From Fuel Oil Gasification, Run No. 4, Sulfur ESCA Scan	161

LIST OF FIGURES (continued)

No. Page

71 Stack Cyclone Material From Fuel Oil Gasification, Run No. 4. Carbon ESCA Scan 162

72 Stack Sampling Train Filter Material From Fuel Oil Gasification, Run No. 4. Surface Broadband ESCA Scan 164

73 Stack Sampling Train Filter Material From Fuel Oil Gasification, Run No. 4. Subsurface Broadband ESCA Scan 165

74 Regenerator Bed Material From Fuel Oil Gasification, Run No. 4. Broadband ESCA Scan 168

75 Regenerator Bed Material From Fuel Oil Gasification, Run No. 4. Sulfur ESCA Scan 169

76 Regenerator Bed Material From Fuel Oil Gasification, Run No. 4. Carbon ESCA Scan 170

77 Annual Surface Wind Roses 177

78 Annual Mean Daily Solar Radiation 178

79 Annual Mean Windspeeds and Resultant Wind Directions 180

80 Isopleths (m x 10^2) of Mean Annual Morning Mixing Heights 181

81 Isopleths (m x 10^2) of Mean Annual Afternoon Mixing Heights 182

82 Horizontal Dispersion Coefficient as a Function of Distance for Pasquill's Stability Types 186

83 Vertical Dispersion Coefficient as a Function of Distance for Pasquill's Stability Types 187

84 SO_2 Concentrations Versus Downwind Distance for Stability Class 1 192

85 SO_2 Concentrations Versus Downwind Distance for Stability Class 2 193

86 SO_2 Concentrations Versus Downwind Distance for Stability Class 3 194

87 SO_2 Concentration Versus Downwind Distance for Stability Class 4 195

LIST OF FIGURES (continued)

No.		Page
88	SO_2 Concentration Versus Downwind Distance for Stability Class 5	196
89	SO_2 Concentration Versus Downwind Distance for Stability Class 6	197
90	SO_2 Concentration Versus Downwind Distance for Stability Class 1 (Plume Rise Retardation Included)	200
91	SO_2 Concentration Versus Downwind Distance for Stability Class 2 (Plume Rise Retardation Included)	201
B-1	Typical Two-Stage Claus Sulfur Plant	224
C-1	Flexicoking Unit	237
C-2	Flexicoking Products	239
C-3	The Gulf HDS Process	242
C-4	Typical RCD Isomax Unit Flow Diagram	245
C-5	BP Residue Desulfurization Process	248
C-6	Resid Hydroprocessing - Standard Oil Co., Indiana	253
C-7	LC-Fining Process Flow Diagram	256
C-8	Residual Ultrafining	258
C-9	Go-Fining	261
C-10	Schematic of the Residfining Process	264
C-11	Residue Hydrodesulfurization Flow Diagram	266
C-12	Hydrodesulfurization, Trickle Flow, Flow Diagram	270
C-13	IFP Resid and VGO Desulfurization Flow Diagram	272
C-14	Demetalization/Desulfurization Flow Diagram	275
C-15	Simplified Flow Diagram for Delayed Coking	278
C-16	VGO/VRDS Flow Diagram	281

LIST OF FIGURES (continued)

No.		Page
C-17	Combined Cycle/Shell Gasification Process	285
C-18	Shell Gasification Power Generation Block Diagram	286

LIST OF TABLES

No.		Page
1	ERCA Pilot Plant Mass Flow Rates	19
2	Mass Flow Rates for FW 10 MW Oil-Fired CAFB Demonstration Plant	21
3	Mass Flow Rates for FW 250 MW Oil-Fired CAFB Design	24
4	Analysis of Fuel Oil Used by ERCA	42
5	Analysis of Bitumen Used by ERCA	44
6	Analysis of Limestone Used by ERCA	44
7	"Typical" Fuel Oil to be Used at the FW Demonstration Plant	46
8	Volatile or Toxic Trace Elements in Oil and Stone	51
9	Comparison of Worst Case Emission Estimates With Air Quality Goals	53
10	Composition of Drainage From Coal Piles	54
11	Summary of Potential Environmental Impacts From the La Palma Station Cooling Towers	59
12	Water Effluent Standards	61
13	Residual Chlorine Recommendations	61
14	Chemicals Used in Recirculative Cooling Water Systems	62
15	Cooling Tower Corrosion and Scale Inhibitor Systems	62
16	Classes of Organic Compounds Eluting in Each Liquid Chromatography Fraction, and Their Approximate IR Detection Limits	81
17	Elemental Sensitivity Factors for the ESCA	83
18	Summary of CAFB Pilot Plant Operating Modes During Test Program	91
19	Representative Pilot Plant Operating Temperatures	91
20	Summary of Sampling Activity	92

LIST OF TABLES (continued

No.		Page
21	Leached Stone Samples	93
22	Field Test Results: Run 1 Fuel Oil Gasification	94
23	Field Test Results: Run 2 Fuel Oil Gasification	94
24	Field Test Results: Run 3 Fuel Oil Gasification	95
25	Field Test Results: Run 4 Fuel Oil Gasification	95
26	Field Test Results: Run 5 Bitumen Gasification	96
27	Field Test Results: Run 6 Bitumen Combustion	96
28	Field Test Results: Run 7 Bitumen Gasification	96
29	Summary of Stack Emissions	97
30	Sample Analyses	106
31	Distribution of Material and Function Groups in Bitumen	112
32	Health and Ecological Effects and MEGS of Organic Compound Classes	113
33	Distribution of Material and Functional Groups in Stack Gas Effluent: Run No. 7	118
34	Distribution of Extractable Organic Material and Functional Groups in Stack Cyclone Particulate: Run No. 5	123
35	Mass Spectrographic and Atomic Absorption Spectrometric Analysis of Stack Cyclone Particulate: Run No. 5	125
36	Surface and Subsurface Concentrations of Stack Particulate Collected During Bitumen Gasification	131
37	Surface Concentrations of Gasifier Bed, Gasifier Cyclone and Knockout Baffle Particulate	134
38	Distribution of Extractable Organic Material and Functional Groups in Spent Stone: Run No. 5	142
39	Surface Concentrations of Spent Stone Particles, Run No. 5	144

LIST OF TABLES (continued)

No. Page

40 Surface Concentrations of Stack Particulate: Run No. 6 147

41 Distribution of Extractable Organic Material and Functional Groups in Stack Cyclone Particulate: Run No. 4 156

42 Mass Spectrographic and Atomic Absorption Spectrometric Analysis of Stack Cyclone Particulate: Run No. 4 157

43 Surface and Subsurface Concentrations of Stack Particulate Collected During Fuel Oil Gasification: Runs 1 to 4 166

44 Surface and Subsurface Concentrations of Particulate Collected on Impactor Substrates: Run No. 4 167

45 Surface Concentrations of Spent Stone Particles: Run No. 4 171

46 Surface and Subsurface Elemental Compositions of Leached Stone Samples 171

47 Relation of Pasquill Stability Classes to Weather Conditions 185

48 National Ambient Air Quality Standards 198

49 Texas Ambient Particulate Standards 199

50 Allowable Particulate Emission Rates For Specific Flow Rates 202

A-1 Mass Flow Rates for FW 10 MW Coal-Fired CAFB Demonstration Plant 206

A-2 Mass Flow Rates for FW 250 MW Coal-Fired CAFB Design 211

A-3 Emission Factors for Coal Drying 214

A-4 Power Plant Coal Ash Compositions 217

A-5 Selected Trace Elements in Ash (ppm) 217

B-1 Summary Description of Flue Gas Desulfurization Processes 228

B-2 Oil-Fired Utility Boilers in the United States Employing Flue Gas Desulfurization 230

B-3 FGD Environmental Impact, tons/yr 231

LIST OF TABLES (continued)

No.		Page
C-1	Economics of Flexicoking Process	240
C-2	Reduced Crudes to HDS Units	241
C-3	Economics of Gulf HDS	242
C-4	Development of Gulf HDS	243
C-5	Yields for RCD Isomax Processing of Kuwait Reduced Crude to 1.0 wt Percent Sulfur	244
C-6	Yields for RCD Isomax Processing of Kuwait Reduced Crude to 0.7 wt Percent Sulfur	244
C-7	Yields for RCD Isomax Processing of Kuwait Reduced Crude to 0.3 wt Percent Sulfur	245
C-8	Economics of RCD Isomax Process	247
C-9	Residue Desulfurization Pilot-Plant Data	249
C-10	Economics of BP Process	250
C-11	HDS Yield Data	252
C-12	Economics of HDS Process	254
C-13	Development of LC-Fining Process	255
C-14	Desulfurization of Kuwait Atmospheric Bottoms	257
C-15	Resid Ultrafining Desulfurization Costs	260
C-16	Resid Ultrafining West Texas Sour Desulfurization Costs	260
C-17	Go-Fining Yields at 90 Percent Desulfurization Level	262
C-18	Economics of Go-Fining	262
C-19	Economics of Residfining Process	264
C-20	Residue HDS Product Yields	267
C-21	Economics of Residue HDS	268

LIST OF TABLES (continued)

No.		Page
C-22	Typical Results From Hydrodesulfurization of Thermal Cracker Gas Oil	269
C-23	Economics of Hydrodesulfurization, Trickleflow Process	271
C-24	Feed Specs and IFP Process Performance	273
C-25	Yields From Kuwait Residue	273
C-26	Typical Economics of IFP HDS Process	274
C-27	Cost Comparison - Desulfurization Versus Demetalization/Desulfurization	277
C-28	Low Sulfur Fuel Oil Production From Arabian Light Residuum	280
C-29	VGO Isomax Plants	282
C-30	Investment Summary	283
C-31	Processing Costs	283
C-32	Typical Product Gas Composition	288
C-33	Power Generation Cost - 200 MW Study	288
D-1	Process Parameters of High Metals Feedstock Desulfurization Techniques	292
D-2	Process Parameters of Residual Oil Feedstock Desulfurization Techniques	293
D-3	Economics for Other Residual Oil Utilization Techniques	296
D-4	Comparative Capital Costs of the CAFB, HDS and FGD Processes	298
D-5	Comparative Operating Costs for the CAFB, HDS and Processes, $/yr	299
D-6	1972 Projected Costs for the CAFB and FGD Processes	300

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SECTION I

EXECUTIVE SUMMARY

OVERVIEW

This document presents the results of a preliminary environmental assessment of the Chemically Active Fluid Bed (CAFB) process. The CAFB is a technique whereby high sulfur, high metal residual oil is vaporized in a fluidized bed of lime to produce a low Btu, low sulfur product gas which is then burned in a conventional boiler to generate electrical energy. Most of the sulfur and metals contained in the oil feed are captured by the lime. This spent lime is subsequently processed to recover sulfur.

At present the only existing CAFB unit is a 2.93 MW pilot plant at the Esso Research Centre, Abingdon, England facility.[1] Foster Wheeler Energy Corporation (FW) is in the final design and procurement stages of a 10 MW retrofit demonstration plant to be constructed in San Benito, Texas, at the La Palma Power Station of the Central Power and Light Company. In addition, FW has developed a conceptual design for a 250 MW commercial scale unit.[2]

Figure 1 is a generalized schematic diagram of the CAFB showing principal unit operations and material flows. Limestone and oil are fed continuously into the gasifier at a Ca (limestone)/S (oil) molar ratio of unity. Limestone ($CaCO_3$) is rapidly converted to lime (CaO) and CO_2 and the lime is maintained in a fluidized state by a preheated air/flue gas mixture. The air input rate is equal to roughly 20 percent of stoichiometric with respect to oil. Fuel oil is consecutively vaporized,

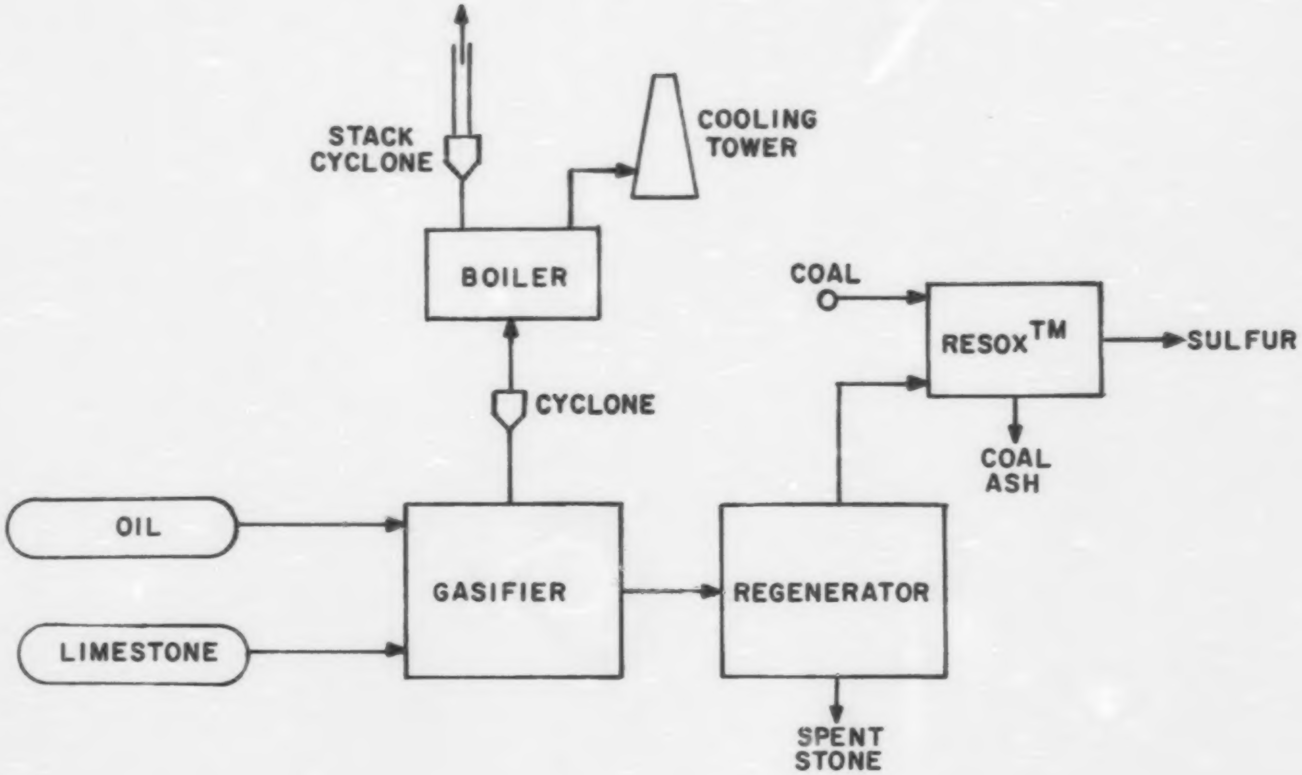
STACK CYCLONE
COOLING TOWER
BOILER
CYCLONE
COAL
RESOX^{TM}
SULFUR
COAL ASH
OIL
GASIFIER
REGENERATOR
LIMESTONE
SPENT STONE

Figure 1. Generalized schematic of the CAFB

oxidized, cracked and reduced at 870°C (1600°F) to produce a low Btu gas. Over 80 percent of the input feed sulfur is removed by the lime. The gas travels from the gasifier through cyclones for particulate removal and then into a boiler for combustion. The boiler flue gas encounters a knockout baffle and another cyclone before entering the stack. Lime is continuously cycled between the gasifier and the regenerator where the roughly 7 percent of the lime which is sulfided in the gasifier is oxidized to CaO. Sulfur dioxide produced in the regenerator is fed to the boiler stack in the pilot plant or reduced to elemental sulfur by coal in the demonstration and commercial plants. Some spent lime is continuously withdrawn from the regenerator and retained for disposal. To maintain sulfur removal efficiency, an equivalent amount of limestone is continuously added to the gasifier.

The CAFB generates pollutants to air, water and land. The primary source of air emissions is the boiler stack but fugitive emissions from feed material storage and handling are also present. Water effluents are similar to those found in conventional combustion systems and include boiler blowdown and cooling tower outputs. Disposal of spent, sulfided limestone is a major environmental problem. A substantial amount of work has and is being carried out to develop an environmentally sound method for stone disposal.[3]

In view of the extensive efforts in the area of solid waste treatment and disposal, the study reported upon here concentrated primarily on air emissions and to a lesser extent on effluents to the other media. Characterization of the multi-media effects of the CAFB involved theoretical engineering and emission calculations for all three CAFB development stages and an extensive field measurement and laboratory analysis program for the pilot plant.

The preliminary theoretical phase of the study utilized CAFB pilot plant data, engineering data developed by FW for the demonstration and commercial units, reports dealing specifically with the CAFB and the general literature to project emission levels from the CAFB demonstration plant and proposed commercial sized facility. Fugitive air emissions were identified as resulting from the storage and handling of oil, limestone and coal, the latter material being used in the FW RESOX^{TM} process to reduce sulfur dioxide emanating from the regenerator to elemental sulfur, and from cooling tower discharges. The fugitive oil vapor emission rate is 104 kg (250 lb)/tank fillup for the demonstration plant and 13 kg/s (103 lb/hr) for the commercial facility. One of the two fuels used at the pilot plant, bitumen, was found possibly to contain polycyclic organic matter (POM); thus emissions from storage of this material, as well as from other oil feeds, must be investigated further. The fugitive dust emission rate from limestone storage and handling is projected to be 3 mg/s (0.024 lb/hr) at the demonstration plant and from 1.9 to 30.6 g/s (13 to 244 lb/hr) at the commercial unit, the extremes corresponding to uncontrolled and baghouse contained crushing emissions. Uncontrolled emissions from coal utilization are estimated to be 6.7×10^{-2} mg/s (5.3×10^{-4} lb/hr) and 0.89 mg/s (7.1×10^{-3} lb/hr) for the demonstration and commercial plants respectively. Cooling tower drift losses at the demonstration plant are estimated to be beween 6 and 50×10^{-4} m^3/s (1.2 and 4.8 cfm) with an evaporative loss of 0.064 m^3/s (135 cfm).

Discharges to ambient water will come from coal pile runoff, cooling tower blowdown and boiler blowdown. Because the CAFB demonstration plant will utilize an existing boiler at the La Palma Power Station, cooling tower and boiler blowdown effluents will be unaffected by CAFB retrofit. At the demonstration plant RESOX^{TM} coal will be stored in a bin; hence no runoff is expected. Runoff from coal storage for the commercial plant will depend upon the specific site, but is estimated to be roughly 212 m^3/year (7500 ft^3/year).

Solid waste disposal requirements will depend upon marketability and disposal options for spent stone, RESOX^{TM} coal ash and elemental sulfur. The demonstration plant will generate 0.07 kg/sec (557 lb/hr) of spent stone and the commercial facility will produce 0.91 kg/sec (7,190 lb/hr) of this material. As noted earlier, disposal of this solid waste is the major environmental problem associated with the CAFB.

The bulk of the sampling and analysis program carried out in conjunction with pilot plant operating during December 1975, was directed toward quantifying stack emissions. Samples were collected during seven separate runs: four fuel oil gasification runs, two bitumen gasification runs and one combustion/startup bitumen run. The field measurement program entailed on-site quantification of SO_2, SO_3, NO_x, H_2S, total particulate and particulate size distributions. In addition, vapor and particulate samples were collected for subsequent chemical analyses. Sulfur dioxide emission rates for fuel oil gasification averaged 0.63 lb/10^6 Btu, 80 percent of the New Source Performance Standard (NSPS) for oil-fired steam generators. Bitumen gasification under conditions of saturated gasifier bed stone (caused by clogging in the gasifier-regenerator stone transfer duct) resulted in an SO_2 emission rate of 1.6 lb/10^6 Btu. Sulfur trioxide emission rates averaged 0.023 lb/10^6 Btu for these same three runs. Total nitrogen oxide emissions ranged from 0.067 to 0.085 lb/10^6 Btu, roughly 25 percent of the NSPS for oil-fired boilers. No significant H_2S was detected in any run. Total particulate emissions ranged from 0.063 to 0.10 lb/10^6 Btu for normal gasification (the NSPS is 0.1 lb/10^6 Btu). During fresh stone feed this rate increased to 0.19 lb/10^6 Btu due to attrition of fresh particles. Particulate size distribution measurements made under gasification conditions for both fuel oil and bitumen feeds indicated roughly one third of the escaping stack particulate is in the respirable size range.

Laboratory analysis of stack particulate employing spark source mass spectrometry (SSMS), atomic absorption spectroscopy (AA) and electron spectroscopy for chemical analysis (ESCA) demonstrated that vanadium, which is bound in a mixture of oxides, is emitted at a rate of almost 90 percent of the EPA established critical value. No other trace element emissions were found to be of concern. Both particulate and gaseous stack samples were also analyzed for organic functional groups by the procedure outlined by the EPA Level 1 protocol. Flue gas analysis results indicated that emissions of hydrocarbons, quinone and carbonyl compounds are potentially of concern.

The results of the field measurement program were used in conjunction with meteorological and topographical characteristics of the San Benito area to project ambient loadings of SO_2 and particulate in the vicinity of the demonstration plant. These projections were compared with State of Texas regulations and found to be in compliance with state requirements.

Finally, the CAFB was compared with alternative residual oil utilization techniques: feed stock desulfurization and flue gas desulfurization (FGD). Of 17 feedstock treatment processes, only three are capable of handling high sulfur and high metals content oil. Comparisons were also developed comparing projected capital and operating costs of the CAFB, FGD and feed stock desulfurization which show that for commercial size facilities, FGD appears to be the most economical of the three options. However, the only existing FGD unit on an oil-fired plant is a MgO scrubber which is almost four times as expensive as published projected costs for FGD units.

CONCLUSIONS

Air

Priority Problems -

- Reduction of stack particulate emissions. Total stack particulate emissions from oil-fired operation of the pilot plant, 30 percent of which are in the respirable size range, were only slightly lower than the New Source Performance Standard (NSPS) for oil-fired boilers. During stone feed/start-up these emissions considerably exceeded the NSPS. The vanadium concentration of these particulates is such that the vanadium emission rate is only slightly lower than the Multi-Media Environmental Goal (MEG) for this element. Under coal-fired operation of the CAFB, proposed for the demonstration plant, the particulate emission problem may be even more pronounced. Foster-Wheeler is designing more efficient cyclones than were installed at the pilot plant. Extensive particulate emission rate measurements at the demonstration plant should be undertaken for all operating modes and for all fuels.

- Reduction of SO_2 emissions during abnormal operating conditions. Blockage of the gasifier-regenerator transfer duct causes saturation of gasifier bed stone and a resultant increase in SO_2 emissions. Operation of the CAFB in this mode for extended time periods should be avoided. Continuous SO_2 monitoring is recommended.

Problems Needing Further Study, But Which Could be Important -

- Detailed investigation of organic stack emissions. Flue gas analyses indicated the possible presence of quinone, carbonyl compounds and aliphatic hydrocarbons in sufficient quantitites to produce ambient concentrations in the neighborhood of the MEG's for these species. Organic emissions are highly dependent on gasifier and boiler operating conditions and should be analyzed with greater specificity than was possible in the present study.
- Measurement of fugitive emissions from oil storage. Polycyclic organic matter (POM) was tentatively identified as a constituent of bitumen. Fugitive air emissions of these compounds from storage and handling of bitumen present a potential environmental hazard. Additional characterization of these emissions is required.

Areas Not Definable Because of Lack of Data -

- Fugitive emissions from RESOX^{TM} coal and ash handling and storage.
- Fugitive emissions from storage and handling of spent stone.

Areas Probably Not Important But Requiring Checking -

- Fugitive emissions from limestone handling.
- Cooling tower emissions.

Areas Definitely Not a Problem -

- NO_x stack emissions. Measurements of NO_x emissions for three separate runs were about 25 percent of the NSPS for oil-fired boilers.
- Trace elements other than vanadium. Stack emission rates of no element other than vanadium approached creating ambient levels on the order of the MEG for that element.

Water

Areas Not Definable Because of Lack of Data -

- Chemical composition of boiler blowdown, cooling tower blowdown and RESOX^{TM} coal pile runoff. Effluents from the first two categories will be unaffected by CAFB retrofit to existing boilers. Coal pile runoff characteristics will be coal type and site specific.

Solid Waste

Priority Problem -

- Environmentally acceptable disposal of spent stone. The demonstration plant will generate 6000 kg/day (13,000 lb/day) and a 250 MW commercial size unit 79,000 kg/day (173,000 lb/day) of sulfided, metal containing lime which must be treated before being disposed of by selling, using as landfill or dumping in the ocean.

Problem Needing Further Study But Which Could be Important -

- Environmentally acceptable disposal of RESOX^{TM} coal ash. Approximately 1600 kg/day (3600 lb/day) of ash will be produced at the demonstration plant and 22,000 kg/day (48,000 lb/day) will be generated at a 250 MW facility.

Area Probably Not Important by Requiring Checking -

- Environmentally acceptable disposal of elemental sulfur. The RESOX^{TM} unit will produce 2600 kg/day (5640 lb/day) of sulfur at the demonstration plant and 35,000 kg/day (76,000 lb/day) at a commercial 250 MW units. Forster-Wheeler plans to sell this material if a market can be found.

REFERENCES

1. Craig, J. W. T., G. L. Johnes, Z. Kowszun, G. Moss, J. H. Taylor, and D. E. Tisdall. Chemically Active Fluid-Bed Process for Sulphur Removal During Gasification of Heavy Fuel Oil - Second PHase. Esso Research Centre, Abingdon, Berkshire, England. U.S. Environmental Protection Agency, Research Triangle Park, N.C. Report Number EPA-650/2-74-109. November 1974. 589 p.

2. Chemically Active Fluid Bed Process (CAFB) Preliminary Process Design Manual. Foster Wheeler Energy Corp., Livingston, N. J. U.S. Environmental Protection Agency, Research Triangle Park, N.C., Contract Number 68-02-2106. December 1975. 185 p.

3. Keairns, D. L., R. A. Newby, E. J. Vidt, E. P. O'Neill, C. H. Peterson, C. C. Sun, C. D. Buscaglia and D. H. Archer. Fluidized Bed Combustion Process Evaluation (Phase 1 - Residual Oil Gasification/Desulfurization Demonstration at Atmospheric Pressure) Volumes I and II. Westinghouse Research Laboratories, Pittsburgh, Pa. U.S. Environmental Protection Agency, Research Triangle Park, N.C. Report Number EPA-650/2-75-027a. March 1975. 578 p.

SECTION II

INTRODUCTION

THE CHEMICALLY ACTIVE FLUID BED PROCESS

The Chemically Active Fluid Bed (CAFB) process was developed by the Esso Research Centre, Abingdon (ERCA), England as a means to generate electrical energy from high sulfur, high metal heavy fuel oil. Fuel oil is fed continuously into a fluidized bed of limestone maintained at 870°C (1600°F) by preheated, substoichiometric air. The fuel oil entering the gasifier is vaporized, oxidized, cracked and reduced to produce a low-Btu, low-sulfur gas which is then burned in a conventional boiler. Sulfur contained in the oil initially forms various gaseous compounds which then react with the bed limestone to yield solid calcium sulfide. The sulfided lime is cycled to a regeneration unit where it is oxidized to produce CaO which is returned to the gasifier and SO_2 which is sent to a sulfur recovery unit. An additional feature of the CAFB process is that the gasifier bed material adsorbs vanadium, nickel and sodium contained in the fuel oil, thus limiting air emissions of these trace elements.

At present the only existing CAFB unit is a 2.93 MW pilot plant at the ERCA facility.[1] Foster-Wheeler Energy Corporation (FW) is in the final design and procurement stages of a 10 MW retrofit demonstration plant[2] to be constructed in San Benito, Texas, at the La Palma Power Station of the Central Power and Light Company. In addition, FW has developed a conceptual design for a 250 MW commercial scale unit.[2]

PROGRAM OBJECTIVES

The objective of this study was to conduct a preliminary environmental assessment of the CAFB. The results of this program provide guidance on measures which must be taken to minimize the environmental impact of the CAFB and suggest follow-up investigations which should be undertaken to insure the environmental acceptability of this process.

To attain these goals, a systematic evaluation of all waste streams from the CAFB was made and a process emissions inventory was compiled. These data were derived from engineering estimates and from an extensive pilot plant field sampling and laboratory analysis program. Emission rates determined for the pilot plant were then used to predict pollutant loadings for the CAFB demonstration plant and for the proposed commercial unit. To provide a long-term overview proposed coal-fired operation of the CAFB is also evaluated. The emissions data are compared with legal requirements and quantifiable health and ecological effects and sources of concern are noted. As part of this latter task, procedures for calculating incremental ambient air loadings are outlined and used to compare projected SO_2 and particulate emissions from the demonstration plant with federal and State of Texas regulations.

In addition to the preparation of the environmental assessment, a preliminary economic assessment was completed which compares the investment and operating costs of a commercial CAFB facility with the costs of alternative residual oil utilization techniques: flue gas desulfurization and feedstock desulfurization.

REPORT ORGANIZATION

Section III provides process descriptions of the ERCA pilot plant, FW demonstration unit and the proposed FW 250 MW commercial facility. Each development stage is broken down into its component unit operations and schematic flow diagrams are developed and waste streams identified.

Emissions estimates developed from engineering evaluations and worst case analyses are presented in Section IV. These projections concentrate on waste streams which were not investigated as part of the field test program.

Section V, which is the crux of this report, describes the field test program and subsequent laboratory analytical studies carried out to characterize stack gas and particulate emissions and solid waste effluent. The results of these studies are presented and intrepreted in terms of potential environmental impact.

Section VI discusses the meteorological and topographical characteristics of a source which control the transport of air pollutants emitted from a stack. The models developed here are then applied to SO_2 and particulate emissions from the La Palma Electric Generating Station.

Conclusions and recommendations for future work are presented in the Executive Summary, Section I.

Appendix A considers coal-fired operation of the CAFB and highlights differences in operating parameters and potential loadings between this mode and oil-firing.

The final three appendixes constitute the comparative economic evaluation of the CAFB. Appendix B discusses the operating characteristics and potential emissions from flue gas desulfurization and from the three feedstock desulfurization procedures capable of processing high metal content residual oil.

Appendix C provides process descriptions and flow diagrams of 15 residual oil desulfurization techniques identified by GCA as being either in commercial operation or potentially viable.

The economic comparison between the CAFB, flue gas desulfurization and residual oil feedstock desulfurization is presented in Appendix D.

REFERENCES

1. Craig, J.W.T., G.L. Johnes, Z. Kowszun, G. Moss, J.H. Taylor, and D.E. Tisdall. Chemically Active Fluid-Bed Process for Sulphur Removal During Gasification of Heavy Fuel Oil - Second Phase. Esso Research Centre, Abingdon, Berkshire, England. U.S. Environmental Protection Agency, Research Triangle Park, N.C. Report Number EPA-650/2-74-109. November 1974. 589 p.

2. Chemically Active Fluid Bed Process (CAFB) Preliminary Process Design Manual. Foster Wheeler Energy Corp., Livingston, N.J. U.S. Environmental Protection Agency, Research Triangle Park, N.C., Contract Number 68-02-2106. December 1975. 185 p.

SECTION III

PROCESS DESCRIPTION

INTRODUCTION

This chapter summarizes, to the degree of detail requisite to an emissions assessment, the technical aspects of the CAFB process. The process descriptions consider each of three development stages, the ERCA pilot plant, the FW 10 MW demonstration unit presently approaching final design specifications and the FW conceptual design of a 250 MW commercial unit. Operating and engineering design parameters have been culled from Esso[1,2,3] and Foster Wheeler[4] reports, from conversations with representatives of these organizations and during a site visit and subsequent sampling operation at the ERCA pilot plant. This section considers oil gasification only; proposed coal gasification is discussed in Appendix A.

OVERVIEW

In the CAFB process heavy fuel oil is consecutively vaporized, oxidized, cracked and reduced in a fluidized bed of lime to produce a low Btu gas. This gas, from which over 80 percent of the sulfur has been removed by the lime, travels from the gasifier through cyclones for particulate removal and then into a boiler for combustion. The boiler flue gas encounters a knockout baffle and another cyclone before entering the stack. Lime is continuously cycled between the gasifier and the regenerator where lime sulfided in the gasifier is oxidized to CaO. Sulfur dioxide produced in the regenerator is fed to the boiler stack or chemically treated to recover sulfur. Some spent lime is continuously withdrawn from the regenerator and retained for disposal. To maintain sulfur removal efficiency, an equivalent amount of limestone is continuously added to the gasifier.

Figure 2 is a schematic diagram of the ERCA pilot plant. Input and output streams to and from each unit operation are labeled and their mass flows and characteristics are given in Table 1. The quantities listed in this table are those projected at steady-state conditions. Parameters will vary during start-up, shut-down and other atypical operating modes. These variations, as pertinent to emission rates, are discussed in the sections describing specific unit operations.

The Foster Wheeler demonstration plant shown schematically in Figure 3 contains, in addition to the basic gasifier and regenerator units, a RESOX^{TM} system for sulfur recovery from the regenerator off gas, a spent solids handling system and a coal storage and feed system for coal gasification. As noted earlier coal gasification will be discussed in Appendix A. Mass flows and stream conditions listed in Table 2 are based on FW design parameters.

The proposed design for a 250 MW CAFB unit is illustrated in Figure 4 The general design is similar to the demonstration plant but more complex in terms of number of unit operations and number of modules required for each unit operation. Stream conditions listed in Table 3 are again based on FW projections.

The remainder of this section treats each CAFB unit operation separately and describes the variation in that unit operation for each stage of development. Waste streams are identified but discussion as to their nature is presented in Sections IV and V.

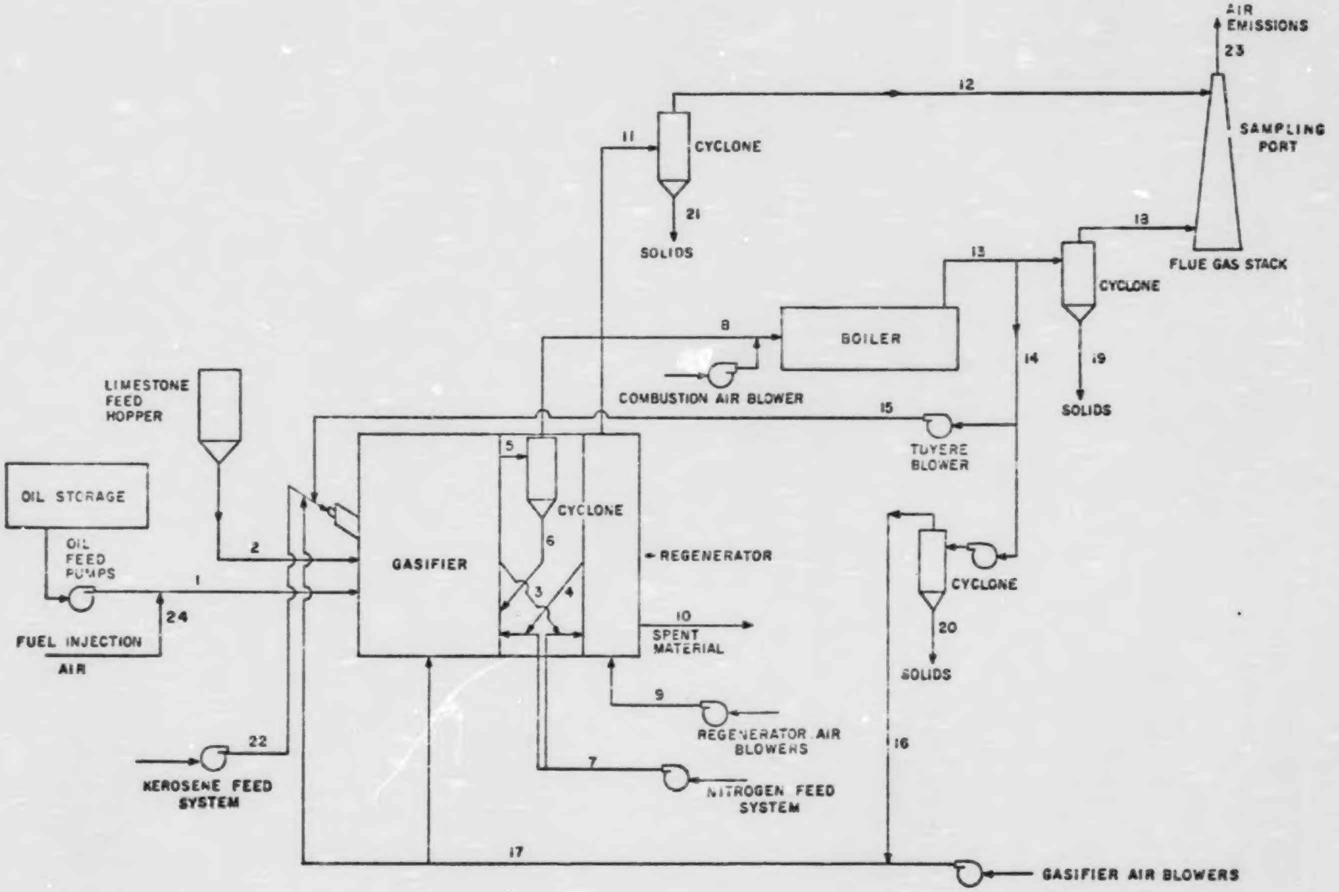
AIR EMISSIONS
23
12
11
CYCLONE
21
SOLIDS
SAMPLING PORT
13
13
FLUE GAS STACK
CYCLONE
8
BOILER
14
19
SOLIDS
LIMESTONE FEED HOPPER
COMBUSTION AIR BLOWER
15
TUYERE BLOWER
5
OIL STORAGE
CYCLONE
OIL FEED PUMPS
2
GASIFIER
6
- REGENERATOR
1
3
4
CYCLONE
24
FUEL INJECTION AIR
10
SPENT MATERIAL
20
SOLIDS
9
REGENERATOR AIR BLOWERS
22
KEROSENE FEED SYSTEM
7
NITROGEN FEED SYSTEM
16
17
GASIFIER AIR BLOWERS

Figure 2. Unit operations flow diagram of the ERCA pilot plant

Table 1. ERCA PILOT PLANT MASS FLOW RATES

Process stream	Mass flow rate, kg/sec	(lb/hr)	Temperature, °C	(°F)
1. Oil feed to gasifier	0.04	(288)	88	(190)
2. Limestone feed to gasifier	0.003	(25)		
3. Gasifier to regenerator stone transfer	0.11	(860)		
4. Regenerator to gasifier stone transfer	0.11	(850)		
5. Product gas to cyclone	0.16	(1,279)	850	(1,560)
6. Cyclone solids return to gasifier				
7. N_2 gas to solids transfer lines	0.0006	(4.5)		
8. Product gas to boiler	0.16	(1,279)	850	(1,560)
9. Air to regenerator	0.01	(65)		
10. Spent solids from regenerator	0.002	(14)		
11. Regenerator off gas to cyclone	0.01	(63)	1,050	(1,920)
12. Regenerator off gas, cyclone to stack	0.01	(63)	1,050	(1,920)
13. Flue gas from boiler	0.50	(4,000)		
14. Flue gas recirculated to gasifier	0.03	(250)		
15. Flue gas to Tuyere Blower	0.02	(125)		
16. Recycled flue gas from cyclone	0.02	(125)		
17. Flue gas and air to gasifier	0.10	(800)		
18. Flue gas to stack	0.50	(4,000)		
19. Solids from boiler flue gas cyclone				
20. Solids from recycled flue gas cyclone				
21. Solids from regenerator off gas cyclone				
22. Start up kerosene to gasifier	0.0005	(4)		
23. Stack emissions	0.50	(4,000)	43	(110)
24. Fuel injection air	0.01	(45)		

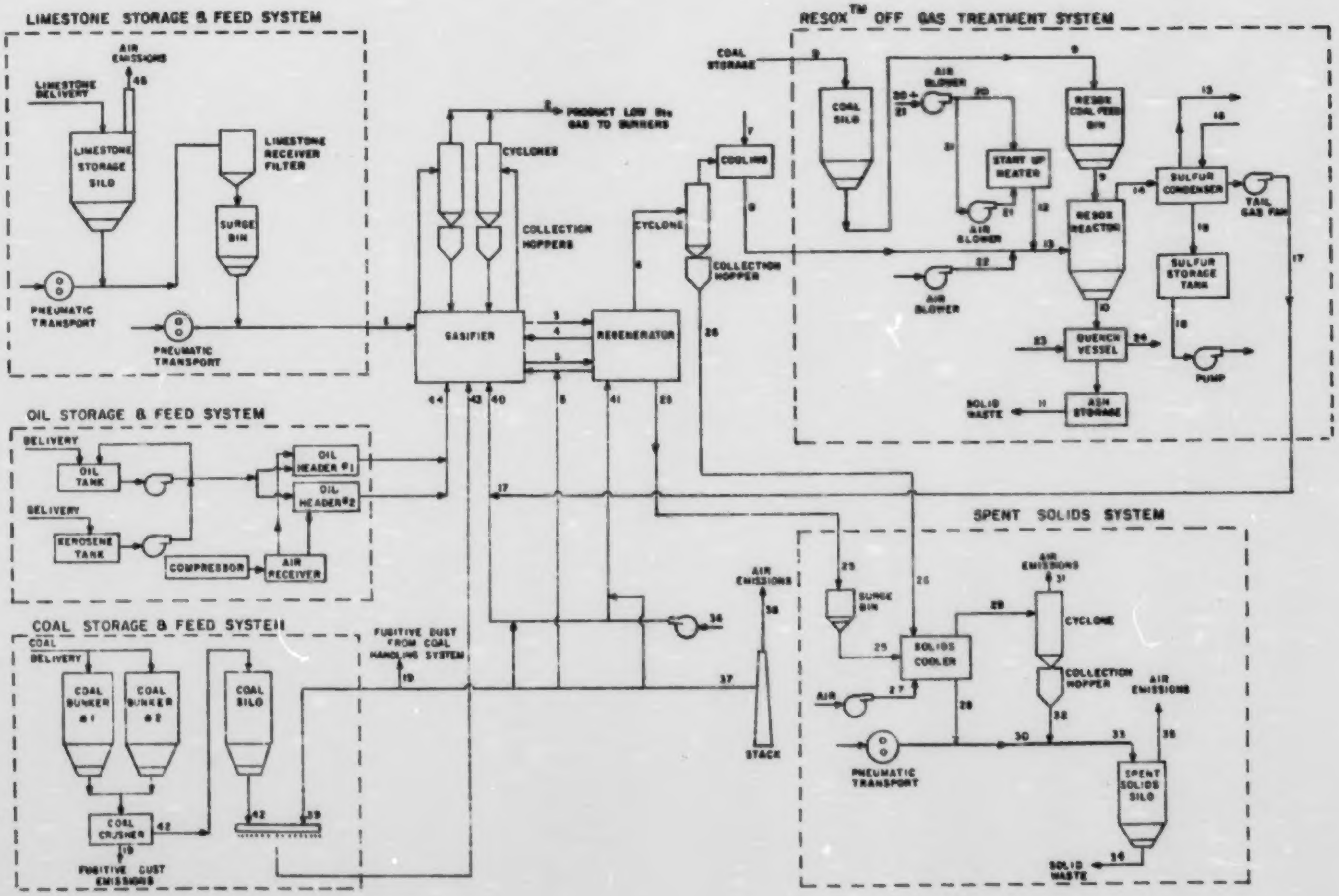
LIMESTONE STORAGE & FEED SYSTEM
LIMESTONE DELIVERY
AIR EMISSIONS
45
LIMESTONE STORAGE SILO
LIMESTONE RECEIVER FILTER
SURGE BIN
PNEUMATIC TRANSPORT
PNEUMATIC TRANSPORT
1
GASIFIER
CYCLONES
COLLECTION HOPPERS
2
PRODUCT LOW Btu GAS TO BURNERS
3
4
5
REGENERATOR
CYCLONE
COLLECTION HOPPER
COOLING
7
8
26
44
43
40
6
41
28
OIL STORAGE & FEED SYSTEM
DELIVERY
OIL TANK
DELIVERY
KEROSENE TANK
COMPRESSOR
AIR RECEIVER
OIL HEADER #1
OIL HEADER #2
17
COAL STORAGE & FEED SYSTEM
COAL DELIVERY
COAL BUNKER #1
COAL BUNKER #2
COAL SILO
COAL CRUSHER
42
19
FUGITIVE DUST EMISSIONS
42
39
FUGITIVE DUST FROM COAL HANDLING SYSTEM
19
34
37
AIR EMISSIONS
38
STACK
RESOX™ OFF GAS TREATMENT SYSTEM
COAL STORAGE
9
COAL SILO
AIR BLOWER
20 + 21
20
21
START UP HEATER
AIR BLOWER
21
12
AIR BLOWER
22
13
9
RESOX COAL FEED BIN
9
RESOX REACTOR
14
SULFUR CONDENSER
15
16
TAIL GAS FAN
18
SULFUR STORAGE TANK
18
PUMP
17
10
23
QUENCH VESSEL
24
ASH STORAGE
11
SOLID WASTE
SPENT SOLIDS SYSTEM
25
SURGE BIN
26
25
SOLIDS COOLER
AIR
27
29
CYCLONE
AIR EMISSIONS
31
COLLECTION HOPPER
32
28
30
33
AIR EMISSIONS
35
PNEUMATIC TRANSPORT
SPENT SOLIDS SILO
36
SOLID WASTE

Figure 3. Unit operations flow diagram of the FW demonstration plant

Table 2. MASS FLOW RATES FOR FW 10 MW OIL-FIRED CAFB DEMONSTRATION PLANT

Process stream	Mass flow rate, kg/sec	(lb/hr)	Temperature, °C	(°F)
1. Limestone to gasifier	0.12	(975)		
2. Product gas from gasifier	7.52	(59,660)	871	(1,600)
3. Gasifier to regenerator stone transfer	4.86	(38,500)		
4. Regenerator to gasifier stone transfer	4.83	(38,275)		
5. Flue gas to pulsed solid transfer lines	0.5	(4,000)	171	(340)
6. Regenerator off-gas: total	0.52	(4,140)	1,038	(1,900)
SO_2	0.09	(724)	1,038	(1,900)
CO_2	0.02	(128)	1,038	(1,900)
N_2	0.41	(3,288)	1,038	(1,900)
7. Water or steam injection	0.07	(575)		
8. Regenerator off-gas after cyclone and cooling	0.52	(4,140)	649	(1,200)
9. Coal to RESOX™ reactor	0.04	(300)		
10. Hot solids from RESOX™ reactor	0.02	(150)	760	(1,400)
11. Waste solids from RESOX™ quench vessel	0.02	(150)	149	(300)
12. Hot air to RESOX™ reactor				
13. Influent gas to RESOX™ reactor				
14. Elemental sulfur from RESOX™	0.03	(253)		
15. Return steam			149	(300)
16. Water to sulfur condenser	0.25	(2,000)	100	(212)
17. RESOX™ tail gas	0.66	(5,250)	160	(320)
18. Condensed liquid sulfur	0.03	(253)		
19. Fugitive dust from coal handling system				
20. Air to start up heater				
21. Air to start up heater				
22. Air to RESOX™ reactor				

Table 2 (continued). MASS FLOW RATES FOR FW 10 MW OIL-FIRED CAFB DEMONSTRATION PLANT

Process stream		Mass flow rate, kg/sec	(lb/hr)	Temperature, ^{o}C	(^{o}F)
23. Cooling water for RESOX^{TM} solid waste		0.01	(50)		
24. Steam from quench vessel					
25. Regenerator spent solids		0.07	(557)		
26. Regenerator off-gas cycloned solids					
27. Air to spent solids cooler		0.69	(5,510)	38	(100)
28. Cooled solids				177	(350)
29. Cooler exhaust to cyclone		0.22	(1,746)	482	(900)
30. Cooled solids to storage					
31. Air emissions from spent solids cooler					
32. Cycloned solids to storage					
33. Solids to storage					
34. Solid waste from storage silo					
35. Air emissions from solids storage silo					
36. Air to gasifier and regenerator		4.50	(35,610)		
37. Flue gas recycled from stack		1.89	(15,000)	171	(340)
38. Boiler stack emissions		23.50	(186,000)		
39. Flue gas to coal distributing conveyor				171	(340)
40. Influent gas to gasifier:	total	5.96	(47,280)		
	Air	3.93	(31,140)		
	Flue gas	1.37	(10,890)		
	Tail gas	0.66	(5,250)		
41. Air and flue gas refenerator		0.56	(4,470)		
42. Coal to distributing conveyor					
43. Coal to gasifier					
44. Oil to gasifier		1.47	(11,630)	121	(250)
45. Fugitive limestone handling emissions					

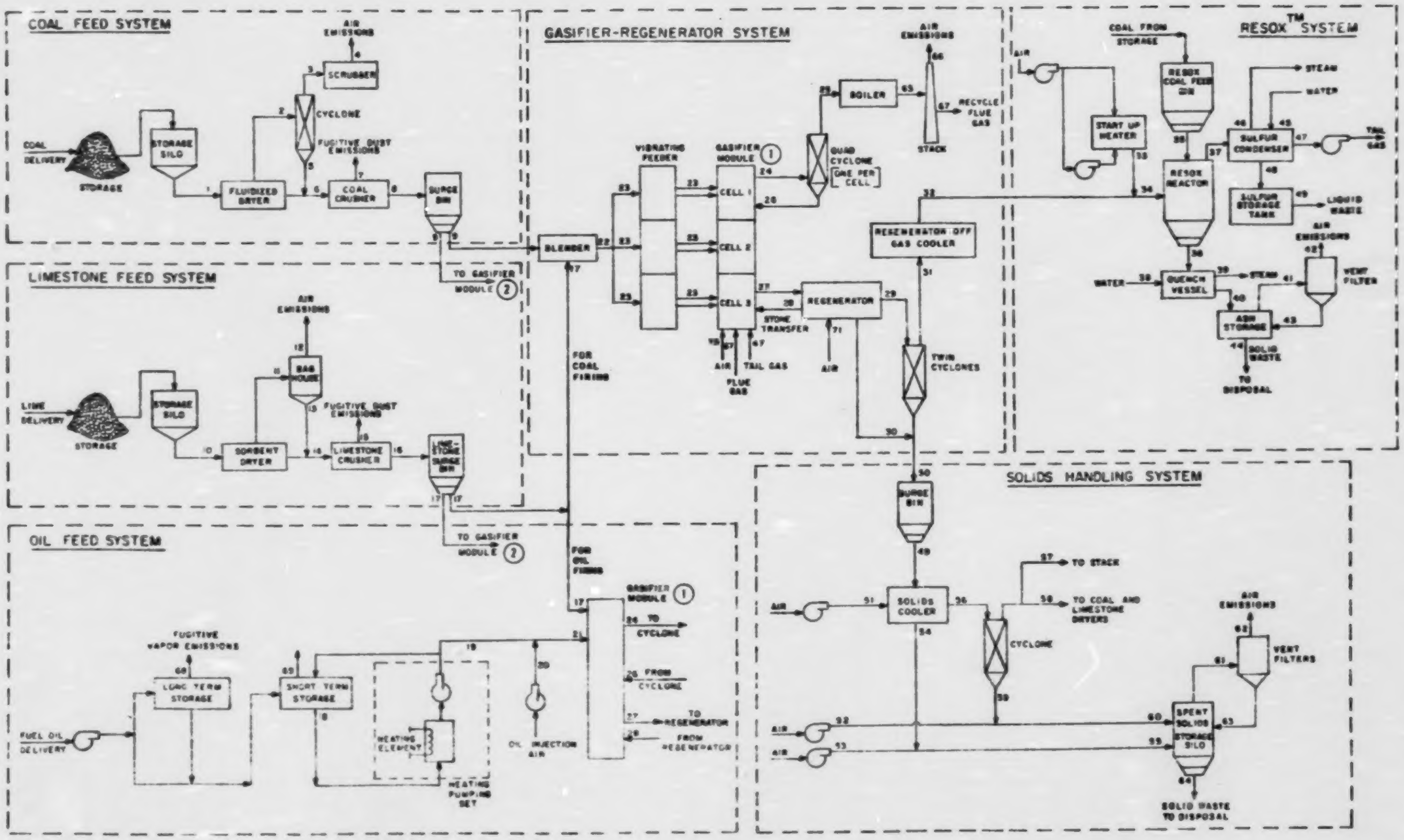
COAL FEED SYSTEM
COAL DELIVERY
STORAGE
STORAGE SILO
FLUIDIZED DRYER
CYCLONE
SCRUBBER
AIR EMISSIONS
FUGITIVE DUST EMISSIONS
COAL CRUSHER
SURGE BIN
TO GASIFIER MODULE ②
LIMESTONE FEED SYSTEM
LIME DELIVERY
SORBENT DRYER
BAG HOUSE
LIMESTONE CRUSHER
LIMESTONE SURGE BIN
OIL FEED SYSTEM
FUEL OIL DELIVERY
FUGITIVE VAPOR EMISSIONS
LONG TERM STORAGE
SHORT TERM STORAGE
HEATING ELEMENT
HEATING PUMPING SET
OIL INJECTION AIR
GASIFIER MODULE ①
TO CYCLONE
FROM CYCLONE
TO REGENERATOR
FROM REGENERATOR
GASIFIER-REGENERATOR SYSTEM
BLENDER
FOR COAL FIRING
FOR OIL FIRING
VIBRATING FEEDER
CELL 1
CELL 2
CELL 3
STONE TRANSFER
AIR
TAIL GAS
FLUE GAS
QUAD CYCLONE ONE PER CELL
BOILER
STACK
RECYCLE FLUE GAS
REGENERATOR
REGENERATOR OFF GAS COOLER
TWIN CYCLONES
RESOX™ SYSTEM
COAL FROM STORAGE
RESOX COAL FEED BIN
START UP HEATER
RESOX REACTOR
SULFUR CONDENSER
STEAM
WATER
TAIL GAS
SULFUR STORAGE TANK
LIQUID WASTE
QUENCH VESSEL
ASH STORAGE
VENT FILTER
SOLID WASTE
TO DISPOSAL
SOLIDS HANDLING SYSTEM
SURGE BIN
SOLIDS COOLER
CYCLONE
TO STACK
TO COAL AND LIMESTONE DRYERS
SPENT SOLIDS STORAGE SILO
VENT FILTERS
SOLID WASTE TO DISPOSAL

Figure 4. Unit operations flow diagram of the FW 250 MW plant

Table 3. MASS FLOW RATES FOR FW 250 MW OIL-FIRED CAFB DESIGN

Process stream[a]	Mass flow rate, kg/sec	(lb/hr)	Temperature, °C	(°F)
10. Limestone to dryer				
11. Off-gas from limestone dryer to baghouse				
12. Air emissions from baghouse				
13. Solids collected by baghouse				
14. Limestone to crusher				
15. Fugitive dust emissions from limestone crusher				
16. Limestone from crusher				
17. Limestone to gasifier modules	1.59	(12,590)		
18. Fuel oil from short term storage				
19. Fuel oil from heating pumping set				
20. Oil injection air				
21. Fuel oil to gasifier modules	19.03	(150,900)	121	(250)
24. Product gas to quad cyclone	97.67	(774,500)	871	(1,600)
25. Product gas to boiler	97.67	(774,500)	871	(1,600)
26. Solids returned from quad cyclone				
27. Gasifier to regenerator stone transfer	63.0	(499,500)		
28. Regenerator to gasifier stone transfer	62.71	(497,240)		
29. Regenerator off-gas to twin-cyclones	6.69	(53,070)	1,038	(1,900)
30. Spent solids from regenerator	0.91	(7,190)		
31. Regenerator off gas from twin-cyclones				
32. Regenerator off gas from cooler			649	(1,200)
33. Air to RESOX™ reactor	2.05	(16,220)		

Table 3 (continued). MASS FLOW RATES FOR FW 250 MW OIL-FIRED CAFB DESIGN

Process stream	Mass flow rate, kg/sec	(lb/hr)	Temperature, °C	(°F)
34. Gas to RESOX^{TM} reactor				
35. Coal to RESOX^{TM} reactor	0.50	(4,000)		
36. Solid waste from RESOX^{TM} reactor	0.25	(2,000)	760	(1,400)
37. Sulfur gas from RESOX^{TM} reactor	0.41	(3,290)		
38. Water to solids quench vessel				
39. Steam from solids quench vessel				
40. Solid waste from quench vessel			149	(300)
41. Gaseous effluent from ash storage				
42. Air emissions from ash storage vent filter				
43. Solids from vent filter to ash storage				
44. Solid waste from ash storage				
45. Water to sulfur condenser			100	(212)
46. Steam from sulfur condenser			149	(300)
47. Tail gas from sulfur condenser recycled to gasifier	8.58	(68,000)	160	(320)
48. Liquid sulfur to storage				
49. Liquid sulfur waste from storage				
50. Solids from regenerator and twin-cyclones				
51. Air to solids cooler			38	(100)
52. Air to spent solids storage				
53. Air to spent solids storage				
54. Solids from solids cooler			177	(350)
55. Solids to storage				
56. Exhaust from solids cooler to cyclone			482	(900)
57. Cycloned solids cooler exhaust to stack				

Table 3 (continued). MASS FLOW RATES FOR FW 250 MW OIL-FIRED CAFB DESIGN

Process stream	Mass flow rate, kg/sec	(lb/hr)	Temperature, °C	(°F)
58. Cycloned solids cooler exhaust to coal and limestone dryers				
59. Cycloned solids to storage				
60. Solids to storage				
61. Exhaust from storage to vent filters				
62. Air emissions from vent filters				
63. Solids from vent filters to storage				
64. Solid waste from storage				
65. Flue gas from boiler to stack	304.91	(2,418,200)		
66. Air emissions from stack	304.91	(2,418,200)		
67. Flue gas recycled to gasifier	17.81	(141,250)	171	(340)
68. Fugitive vapor emissions from long term fuel oil storage	0.01	(103)		
69. Fugitive vapor emissions from short term fuel oil storage	0.01	(103)		
70. Air to gasifier	50.95	(404,020)		
71. Air to regenerator	7.31	(58,000)		

[a] Process streams 1 through 9, 22 and 23 are applicable to coal-firing and are presented in Appendix A.

FUEL FEED SYSTEM

ERCA Pilot Plant

Fuel Oil — Fuel oil, stored in an external vented storage tank, is passed through an oil immersion heater before being fed to the gasifier.

Bitumen — Bitumen is stored in a four-compartment tank car having a total capacity of 63.6 m^3 (18,000 imperial gallons). Each compartment is heated with gas oil to bring the bitumen to a temperature which will allow it to flow through the feed lines to the gasifier. The gas oil is stored in a 0.18 m^3 (50 imperial gallon) drum.

Kerosene — Kerosene, used as the startup fuel, is stored in an underground 1.8 m^3 (500 imperial gallon) tank from which it is pumped into the fuel oil feed line.

Emissions — The principal emissions from the fuel feed systems are fugitive vapors escaping from storage tank venting systems. In addition, there may be some leakage of liquid fuels during tank fillup (evidence of leakage was noted about the bitumen tank car). Seepage of this sort is localized and easily confinable.

FW Demonstration Plant

Oil and Pitch — Fuel will be delivered to the plant in heated tank cars and stored in a heated 378.5 m^3 (100,000 gallon) tank. Oil is transferred to the gasifier through two headers located adjacent to the gasifier.

Kerosene — Startup fuel is stored in a separate tank and fed to the gasifier through the oil delivery system.

Emissions — Considerations similar to those in the pilot plant system apply here.

FW 250 MW Unit

Fuel Oil — Fuel oil will be delivered by rail in heated tank cars and pumped into short-term and long-term storage tanks. The long-term tank will be designed for 3 weeks storage and the short-term tank for 2 days supply. Oil from the short-term tank will be pumped to a heating/pumping set which will bring the oil to the temperature and pressure required in the gasifier oil supply header. A portion of the feed oil will be returned to the short-term storage tank for temperature control.

Kerosene — This system is similar to that of the demonstration plant.

Emissions — Considerations similar to those in the pilot plant apply here.

LIMESTONE HANDLING SYSTEM

ERCA Pilot Plant

Limestone is delivered to the plant in bags and transferred to a ground level hopper. A pneumatic system transports the stone to an upper hopper from which it is periodically dropped into a weigh feeder. The limestone then moves by gravity into the gasifier. Fugitive dust will escape during hopper loading and stone feed.

FW Demonstration Plant

Limestone will be delivered to the plant by truck and offloaded to a storage bunker designed to contain a 13 day stone supply. Baghouse filters attached at the top of the bunker are designed to abate fugitive dust emissions. Limestone is to be transported through a rotary feeder-airlock valve, a pneumatic transfer line and finally into a pressurized surge bin from which another rotary feeder-airlock valve will inject stone into the gasifier. Fugitive dust emissions will be generated by these limestone handling operations.

FW 250 MW Unit

High calcium limestone will be conveyed to either a 6 day supply pile or to a dead storage pile containing a 30 day supply. Sorbent will be dried in a fluidized dryer prior to crushing. During start-up, hot gases for drying will be provided by combusting coal in the furnace section of the dryer. At steady state operation, hot exhaust from the spent solids cooler will be used for coal drying. The dried sorbent will then be transferred to a limestone crusher. Crushed limestone, sized at less than than 3.2 mm (1/8 in.), will then be transferred to the gasifier modules. As presently designed this group of unit operations will produce fugitive dust emissions from limestone transfer, storage and crushing and fugitive gases from coal combustion.

GASIFIER

General Description and Chemistry

The basic components of the CAFB process are the gasifier and regenerator. Figure 5 schematically illustrates the interaction between these unit operations. Limestone and fuel oil are added to the gasifier at an approximate Ca:S molar ratio equal to one. ERCA pilot plant studies indicate a sulfur removal efficiency (SRE) of at least 80 percent based on this stone/feed makeup ratio. Air is fed into the gasifier at 20 to 23 percent stoichiometric in order to partially oxidize the fuel oil and produce a temperature 871°C (1600°F) suitable for vaporization and cracking of the fuel. Flue gas from the boiler at approximately 171°C (340°F) is recirculated to the gasifier for temperature control. A product gas is produced which has a heating value of approximately 1665 kcal/kg (3000 Btu/lb). The predominant reactions taking place in the gasifier are as follows:

$$\text{Oil thermal cracking} \rightarrow C + H_2 + \text{hydrocarbons} + H_2S + CS_2 + COS$$

$$CaO + H_2S \rightleftharpoons CaS + H_2O$$

$$CaO + COS \rightleftharpoons CaS + CO_2$$

$$CaO + 1/2CS_2 \rightleftharpoons CaS + 1/2CO_2$$

The equilibria for these reactions are well to the right. Approximately 7 percent of the input limestone as calcium oxide is reduced to calcium sulfide on each pass of stone through the gasifier.

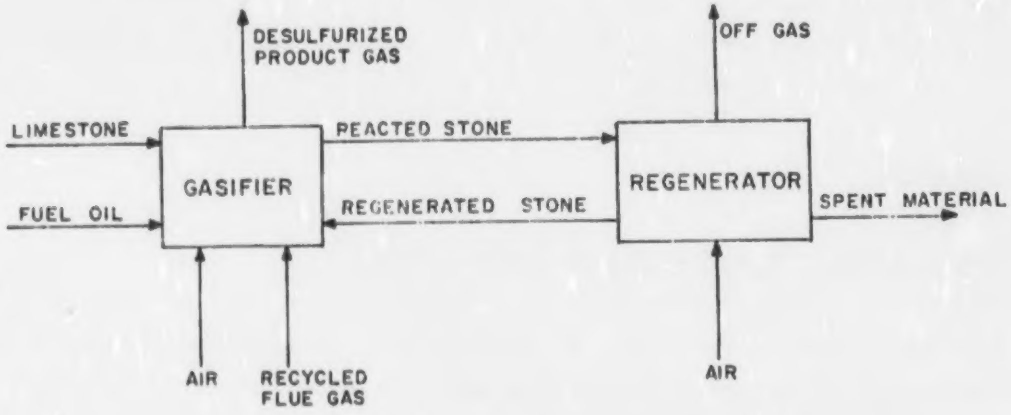
DESULFURIZED PRODUCT GAS
OFF GAS
LIMESTONE
FUEL OIL
GASIFIER
REACTED STONE
REGENERATED STONE
REGENERATOR
SPENT MATERIAL
AIR
RECYCLED FLUE GAS
AIR

Figure 5. Gasifier-regenerator schematic

ERCA studies also indicate that approximately 95 percent of the vanadium, 75 percent of the nickel and 40 percent of the sodium contained in the fuel oil are captured by bed stone.

Startup is accomplished by heating the unit slowly by kerosene combustion until the appropriate gasification temperature is reached. Fresh limestone is added toward the end of this period until the requisite bed depth is attained. During limestone addition, stone attrition and calcining, which leave the bed in the form of CaO, result in appreciable particulate and CO_2 formation.

A possible upset condition, which in fact occurred several times during the GCA sampling program at ERCA, is clogging of the gasifier-regenerator stone transfer system. This situation results in saturation of the gasifier stone with the consequent decrease in SRE.

ERCA pilot plant

The process streams and mass flow rates associated with the ERCA pilot plant are shown in Figure 2 and listed in Table 1. These quantities are based upon a product gas flow rate of 0.16 kg/s (1279 lb/hr).

The gasifier used in the pilot plant is circular in plan and consists of a cylindrical and conical section over its height. It is 0.73 m (28 in.) in diameter at the top and has a total volume of 1.08 m^3 (38.1 ft^3). Fuel oil enters through a single entrance port situated above the air distribution mechanism. The quantity of air introduced into the gasifier is 20 to 23 percent of the stoichiometric amount required to completely oxidize the carbon in the fuel oil. In addition flue gas is recirculated to the gasifier for temperature control. Product gas passes through a cyclone adjacent to the gasifier before entering the boiler. A solids drain transports collected particulate matter back into the gasifier. ERCA studies have defined the most important factors influencing SRE to be bed depth and stone sulfur content. The static bed depth should be greater than 38 cm (15 in.) and the content of sulfur in the stone less than 4 percent. Recent analysis by ERCA indicates that water added to the gasifier can be detrimental to SRE.

FW Demonstration Plant

The specific process streams and mass flow rates specified for the Foster Wheeler design are shown in Figure 3 and listed in Table 2. The quantities are based upon development of 8.3 kg/s (65,800 lb/hr) of product gas with a higher heating value of 1735 kcal/m^3 (195 Btu/ft^3)

The gasifier proposed by Foster Wheeler has a floor area of 14.6 m^2 (149 ft^2) and an internal height of 3.66 m (12 ft). Limestone will be fed into the gasifier from an adjacent pressurized surge bin of 1.4 m^3 (50 ft^3) volume. A variable speed rotary feeder will inject limestone at a height of approximately 1.2 m (4 ft) above the level of the chamber floor. The expanded limestone bed depth will be maintained at 0.91 m (3 ft). The particle diameter of the limestone feed ranges from 0.6 to 3.2 mm (0.024 to 0.126 in.).

Fuel oil will be fed into the gasifier chamber by way of two headers, both of which subdivide into 15 injection nozzles. Each nozzle enters into 1 of 30 oil injection combustion pits which are spaced evenly over the gasifier floor. The pits are square in plan with an area of 0.1 m^2 (1 ft^2) and a depth of 12.7 cm (5 in.). Air will be injected at a rate of 22 percent of the stoichiometric amount required for complete combustion of the fuel oil. Flue gas and RESOX™ tail gas are to be recirculated to the gasifier for temperature control and removal of residual sulfur gas, respectively.

The gaseous mixture will enter the plenum below the gasifier floor before entering the nozzle distribution system. Five hundred and ninety stainless steel air/flue gas nozzles are distributed evenly over the floor area at a spacing of 15.2 cm (6 in.). Four nozzles enter through the bottom of each oil injection combustion pit in order to provide uniform interaction between the fluid limestone bed and fuel oil.

FW 250 MW Unit

The gasifier will consist of two modules comprised of three cells each. Each cell is designed as a mockup of the gasifier/regenerator unit proposed for the 10 MW demonstration plant. An individual cell has a floor area of 23.2 cm^2 (250 ft^2) as compared to a floor area of 13.9 m^2 (149 ft^2) designed for the 10 MW demonstration plant.

Product gas from each cell will pass through a quad cyclone (four cyclones in parallel) before firing the steam generating unit. Refractory lined return pipes will convey collected solids back to the cells by gravity.

Each gasifier module will be approximately 17.7 m (58 ft) high with the two bottom cells 6.1 m (20 ft) and the top cell 5.5 m (18 ft) in height. Each gasifier cell will be 3.34 m (11 ft) wide and 7.54 m (24.75 ft) long. The vertical distance from the air distribution grid to the ceiling of the cell is to be 4.6 m (15 ft). Ducts leading to the quad cyclones exit from the top of each gasification cell. During gasification, oil will be injected into each cell through 50 injection pipes. The oil injection combustion pits and air distribution system are as described for the 10MW demonstration plant. Each oil injection pipe will serve 0.5 m^2 (5 ft^2) of the total cell floor area of 23.2 m^2 (250 ft^2).

REGENERATOR

General Description and Chemistry

The regeneration step is accomplished in a reaction vessel adjacent to the gasifier. Limestone comprised of approximately 93 percent CaO and 7 percent CaS is fed to the regenerator where it reacts with a stoichiometric quantity of air by the reactions:

$$CaS + 3/2\ O_2 \rightleftharpoons CaO + SO_2$$

$$CaS + 2O_2 \rightleftharpoons CaSO_4$$

$$CaS + 3CaSO_4 \rightleftharpoons 4CaO + 4SO_2$$

In addition, carbon deposited on the stone during gasification (approximately 0.3 percent by weight) is oxidized to CO_2.

The off gas from the regenerator contains SO_2, CO_2 and N_2 derived from the influent air. Spent solid material consists of approximately 94 percent CaO, 2.5 percent $CaSO_4$, and 3.5 percent CaS. In the Foster Wheeler demonstration plant and 250 MW unit, off gas will be transported to the RESOX™ system for recovery of elemental sulfur, and spent solids will be conveyed to a solids cooler and storage bin. These components are shown schematically in Figures 3 and 4. At the ERCA pilot plant regenerator off gas passes through a cyclone and then into the boiler stack. The stone transfer rate indicated in Tables 1 and 2 for the ERCA pilot plant and the FW demonstration plant are based on a factor of 3.3 kg of stone transferred per kg of oil fed to the gasifier. The SO_2 volume in the regenerator off gas is equivalent to 0.031 kg of elemental sulfur per kg of oil input to the gasifier.

ERCA Pilot Plant

The regenerator used in the ERCA pilot plant is contained in a refractory concrete block. The axis of the regenerator is offset 0.69 m (27 in.) from the central axis of the gasifier. The diameter of the regenerator is 0.25 m (10 in.) at the top and the height of the unit is 3.35 m (132 in.). A nitrogen gas system is used to pulse solids through transfer pipes which run between the gasifier and regenerator at the bottom of each unit.

Regenerator off gas flows through a cyclone for particulate removal and then directly to the stack for atmospheric discharge. Spent solid material is stored during pilot plant operation and subsequently discarded.

FW Demonstration Plant

The regenerator will be housed within the same structure as the gasifier, the two vessels being separated by a partition. The plan area of the regenerator is 1.8 m^2 (19.3 ft^2) and the height is 3.66 m (12 ft). Stone transport is to be accomplished by way of two transfer conduits in the separation wall. A set of flue gas nozzles will be included in each transfer slot in order to maintain continuous material flow through the duct. A division wall within the regenerator prevents short circuiting of spent stone back into the gasifier prior to complete regeneration.

Regenerator off gas will pass through a cyclone and then into the RESOX^{TM} system. Spent stone will be sent to a solids handling system for eventual disposal or reuse.

FW 250 MW Unit

The regenerator units will be cast monolithically with the gasifier cells in each module. A solids transfer system will be housed in the gasifier/regenerator division wall in order to pulse solids between the two chambers. The floor area of each regeneration unit (one per gasifier cell) will be 0.87 m (34.4 in.) by 3.3 m (129.4 in.). The regenerator off gas containing SO_2 will pass through two refractory lined cyclones prior to entering the RESOX^{TM} reactor. Collected solids and spent material will be transferred to a solids cooler and stored.

Emissions

Of the three CAFB development projects only the ERCA pilot plant regenerator produces waste streams which enter the environment directly. The regenerator off gas stream is composed primarily of SO_2, CO_2 and N_2. The spent stone is a mixture of CaO, CaS, $CaSO_4$, carbonaceous material and trace metals in various chemical forms.

SPENT SOLIDS HANDLING SYSTEM

FW Demonstration Plant and 250 MW Unit

The spent solids handling system designed by Foster Wheeler will confine solids continuously withdrawn from the regenerator and particulate matter collected by the regenerator off gas cyclones. The combined material will be cooled to approximately 177°C (350°F) by heat exchange with air in a fluidized bed cooler. Cooled solids will then be transported by pneumatic conveyor to a storage silo from which spent material will eventually be removed in closed dump trucks to disposal sites.

Emissions

Hot air from the fluidized bed cooler will pass through a cyclone before becoming a waste stream to the atmosphere. This stream will be primarily nitrogen and oxygen but may also contain CO_2, SO_2 and lime particulate. The solid waste stored in the silo will be primarily CaO with small amounts of CaS, $CaSO_4$ and trace quantities of metallic oxides and carbonaceous material.

FW RESOX^{TM} OFF GAS TREATMENT SYSTEM

Demonstration Plant and 250 MW Unit

The RESOX^{TM} system is a proprietary system developed by Foster Wheeler to reduce SO_2 to elemental sulfur. Details of the process are not in the public domain and thus only a cursory description of the unit operations involved can be given. Regenerator off gas passes through a cyclone and is then cooled to 650°C (1100°F) before entering the RESOX™ reactor where the SO_2 in the off gas reacts with anthracite coal (carbon content ~ 92 percent) via the reaction:

$$SO_2 + C \rightleftharpoons CO_2 + S$$

Preheated air is fed to the reactor to maintain the temperature at about 760°C (1400°F). Foster-Wheeler estimates that 70 percent of the influent SO_2 is reduced to elemental sulfur. Coal ash from the reactor is quenched with water and stored for later disposal. Gaseous elemental sulfur formed in the reactor is condensed and the resultant liquid sulfur is stored for possible resale. Tail gas exiting from the condenser will be returned to the gasifier for reaction with limestone.

Emissions

The principal waste stream associated with the RESOX™ system is coal ash remaining after reduction in the reactor. Present plans call for storage of the ash and subsequent disposal. In addition, fugitive dust may be generated during coal handling and storage.

BOILER

ERCA Pilot Plant

Product gas from the gasifier undergoes combustion in a 2.9 MW (10 x 10^6 Btu/hr) pressurized water tube boiler. A mechanical draft cooling tower is used to dissipate cooling water circulating to the condenser. Boiler flue gas containing roughly 5 percent oxygen exist through a knock-out baffle and cyclone before entering the boiler stack. About 5 percent of the boiler flue gas is bled off through a baghouse unit and returned to the gasifier for temperature control. The remaining flue gas exits the top of the stack at a rate of approximately 5.7 m^3/s (1200 ft^3/min).

FW Demonstration Plant

Product gas from the gasifier will undergo combustion in steam generator Unit No. 4 of the La Palma Power Station. This 20 MW oil and gas fired unit will be retrofit with two burners designed to handle 7.52 kg/s (59,660 lb/hr) of product gas, thus allowing half load firing with product gas from the 10 MW CAFB or full load firing using both natural gas and product gas. Unit No. 4 produces up to 31.5 kg/s (250,000 lb/hr) of steam at 446°C (835°F) and 4.76×10^6 Pascals (675 psig). Preheated air enters the boiler at 232°C (450°F) and flue gas enters the boiler stack, after passing through the air preheater heat exchanger at 191°C (375°F). Flue gas will be recycled to the gasifier for temperature control at the rate of 0.66 kg/s (5,250 lb/hr). The remainder of the flue gas, approximately 34.1 kg/s (270,000 lb/hr) will exit through the power station stack.

FW 250 MW Unit

A boiler has not yet been selected for the utility retrofit.

Emissions

Boiler flue gas is the primary source of air emissions from all CAFB units and is treated in detail in Sections IV and V of this report in which actual measurements of pilot plant stack emissions are discussed and projections given for the demonstration plant and 250 MW unit. Other sources of atmospheric and water emissions are the cooling towers and boiler blowdown and treatment associated with each plant.

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1. Craig, J.W.T., G.L. Johnes, G. Moss, J.H. Taylor, and D.E. Tisdall. Study of Chemically Active Fluid Bed Gasifier for Reduction of Sulphur Oxide Emissions (Final Report, June 1970 to March 1972). Esso Research Centre, Abingdon, Berkshire, England. U.S. Environmental Protection Agency, Research Triangle Park, N.C. Report Number EPA-R2-72-020. June 1972. 334 p.

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3. CAFB Operators Manual. Esso Research Centre, Abingdon, Berkshire, England. November 1975. 44 p.

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SECTION IV

EMISSIONS ESTIMATES

INTRODUCTION

This section and the next probe the chemical and physical properties of the waste streams identified in the preceding section. The emissions assessment discussion is divided into two parts: the first, presented here, contains emissions estimates for waste streams not sampled by GCA; the second half, described in Section V, consists of a detailed presentation of the protocols and results of the field test program conducted by GCA at the ERCA CAFB pilot plant.

The emissions estimates calculated in this section are derived from several sources:

- CAFB pilot plant process data and log sheets;
- Emissions projections prepared by Foster-Wheeler for the demonstration and commercial CAFB plants;
- Reports dealing specifically with the CAFB process;
- General literature on process emissions.

Studies by ERCA,[1,2] Westinghouse,[3,4] Foster Wheeler[5] and others have concentrated on two areas: stack SO_2 emissions and sulfate, sulfide and trace metal concentrations of spent regenerator stone. In addition, these reports contain detailed discussions of the environmental and economic acceptability of various options proposed for stone disposal.

Reports by EPA contractors dealing with spent stone from fluidized-bed combustion of coal[6,7] provide the basis for stone characterization reported in this study. These workers have concentrated on sulfur and trace metal content of stone. To complement these studies GCA collected spent stone samples and had them analyzed for organic functional groups and surface elements. These results are presented in Section V.

Although fugitive air emissions from oil, coal, ash and limestone storage and handling and water emissions from cooling towers and boiler effluent are not unique to the CAFB, they are discussed here to provide a complete emissions assessment. Analyses of these emissions are based on general systems[8] with some amplification of factors peculiar to the CAFB or to conditions associated with the San Benito area. In addition, worst case analyses for flue gas emissions, based upon input material composition and feed rates tabulated in the next subsection, are presented and compared to legal requirements and known health and ecological effects information where appropriate.

INPUT MATERIALS

During the latest operation of the ERCA pilot plant, Run No. 10 November-December 1975, both No. 6 fuel oil (atmospheric bottoms) and bitumen (vacuum bottoms) were gasified in the CAFB. The fuel oil, from Venezuelan crude, had been used in previous ERCA runs. The bitumen had not. Chemical and physical analyses of both fuels are presented in Tables 4 and 5. Table 6 presents an extensive breakdown of elements found in the limestone used during Run No. 10. The concentrations reported in this table were determined by ERCA using atomic absorption spectroscopy (AA) and neutron activation analysis (NAA). In addition, Figure 6 is an ESCA* spectrum of the limestone particulate surface. Surface abundances are also listed in Table 6.

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*See Section V.

Table 4. ANALYSIS OF FUEL OIL USED BY ERCA

Elements and properties	Concentration or value
C[a]	85.3 ± 0.2 %
H[a]	11.3 ± 0.1 %
S[a]	2.5 ± 0.01 %
N[a]	0.35 ± 0.02 %
V[a]	307 ± 2.2 ppm
Ni[a]	41 ± 2.5 ppm
Na[a]	39 ± 3.3 ppm
Ca[b]	26 ± 3.1 ppm
Si[b]	20 ± 3.9 ppm
K[b]	17 ± 7.8 ppm
Sn[b]	17 ± 9 ppm
Cd (In)[c]	7 ± 1.4 ppm
Pb[b]	3.6 ± 0.2 ppm
Zn[b]	2.7 ± 0.5 ppm
Fe[a]	2.7 ± 0.33 ppm
Al[b]	2.1 ± 0.6 ppm
Cr[c]	1.4 ± 0.14 ppm
Mg[d]	1 - 10 ppm
Mn[c]	0.9 ± 0.18 ppm
Sb[b]	0.73 ± 0.31 ppm
P[b]	0.47 ± 0.18 ppm
Mo[b]	0.44 ± 0.36 ppm
Cu[b]	0.39 ± 0.13 ppm

Table 4 (continued). ANALYSIS OF FUEL OIL USED BY ERCA

Elements and properties	Concentration or value
As[d]	0.3 - 3 ppm
Rb[b]	0.27 ± 0.10 ppm
Ti[b]	0.25 ± 0.15 ppm
B[b]	0.22 ± 0.08 ppm
F[b]	0.22 ± 0.015 ppm
Co[c]	0.2 ± 0.04 ppm
Ba[b]	0.16 ± 0.01 ppm
Sr[b]	0.092 ± 0.088 ppm
Cs[b]	0.090 ppm
Cl[d]	0.06 - 0.6 ppm
Ga[b]	0.024 ± 0.009 ppm
Te[c]	<1 ppm
Ge[d]	<0.074 ppm
Specific gravity[a]	0.958 ± 0.001
Conradson Carbon[a]	10.8 ± 0.3
Asphaltenes[a]	5.45 ± 0.22 %
Heating value[e]	10.3 kcal/gm (18,530 Btu/lb)

[a] Reference 2, p. 539.

[b] By Spark Source Mass Spectrometry (SSMS); performed for PMB/EPA by Northrup Services, Inc.

[c] By Neutron Activation Analysis (NAA); performed for ERCA by the U.K. Atomic Energy Establishment, Harwell.

[d] By Atomic Absorption (AA) spectroscopy; performed by ERCA.

[e] From ERCA.

Table 5. ANALYSIS OF BITUMEN USED BY ERCA

Elements and properties	Concentration or value
S[a]	3.75 %
V[a]	550 ± 50 ppm
Ni[a]	74 ppm
Phenolics[b]	Present
Aromatics - possibly POM[b]	Present
Conradson Carbon[a]	9.71
Specific gravity[a]	1.0185
Heating value[a]	9.9 kcal/gm (17,900 Btu/lb)
Viscosity[a]	376.3 cs (135°C) 203.6 cs (150°C) 75.0 cs (175°C)

[a] Private communication, ERCA.

[b] From LC/IR organic functional group analysis (see Section V) performed by EPA and Battelle Columbus Laboratories.

Table 6. ANALYSIS OF LIMESTONE USED BY ERCA[a]

Element	Concentration
Ca	71.5%
Mg[b]	0.2 - 2%
Si[b]	600 - 6000 ppm
Al[b]	200 - 2500 ppm
Fe[b]	200 - 2000 ppm
Sr[b]	100 - 1000 ppm
K[b]	100 - 1000 ppm
Ba[b]	30 - 300 ppm
Cl[b]	10 - 100 ppm
Na[b]	10 - 100 ppm
Ni[b]	< 50 ppm
Cd or In[c]	29 + 6 ppm
Mn[c]	22 ± 1 ppm
Sb[c]	< 10 ppm
I[b]	1 - 10 ppm
P[b]	1 - 10 ppm
Ti[b]	0.6 - 6 ppm
Te[c]	2 + 0.2 ppm
Cr[c]	2 ± 0.4 ppm
La[b]	0.3 - 3 ppm
Co[c]	0.3 ± 0.01 ppm
V[b]	0.06 - 0.6 ppm
Surface O[d]	49.5 %
Surface C[d]	38.9 %
Surface Ca[d]	11.6 %
$CO_3^{=}/C$[d]	0.5

[a] All results except surface elements and $CO_3^{=}/C$ from ERCA.

[b] Atomic Absorption (AA) spectroscopy.

[c] Neutron Activation Analysis (NAA) performed the U.K. Atomic Energy Establishment, Harwell.

[d] Electron Spectroscopy for Chemical Analysis (ESCA) (see Figure 6).

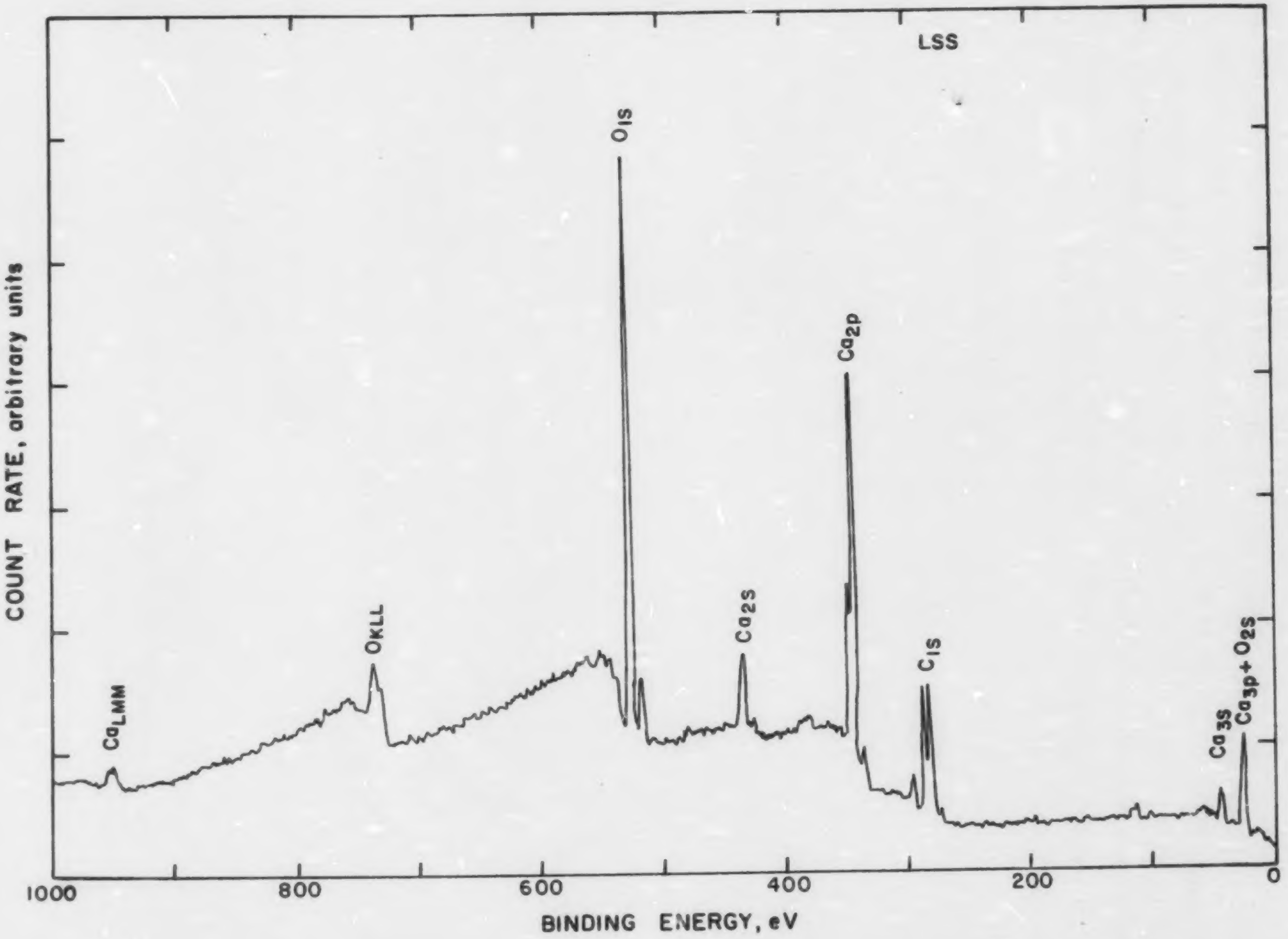

Figure 6. Limestone feed. Broadband ESCA scan

These data are used throughout this report to make worst case emission analyses, engineering estimates of emission rates and to normalize the field program results obtained at the pilot plant. Finally, typical characteristics of the fuels to be utilized in the FW demonstration plant are presented in Table 7 to provide a basis for projected emissions from that facility and from the 250 MW unit.

Table 7. "TYPICAL" FUEL OIL TO BE USED AT THE FW DEMONSTRATION PLANT

Elements and properties	Concentration or value
C	84.43%
H	10.58%
S	2.67%
O	1.68%
N	0.37%
Moisture	0.2%
Ash	0.07%
Specific gravity	0.9765
Heating value	10.3 kcal/gm (18,423 Btu/lb)

FUGITIVE AIR EMISSIONS FROM OIL STORAGE AND HANDLING

Fugitive evaporative losses from liquid storage tanks depend on several factors:

- Vapor pressure of the liquid
- Temperature variations within the tank
- Height of vapor space
- Tank diameter
- Filling and emptying frequency
- Condition and type of tank.

For fixed roof storage tanks the largest emissions result from emptying and filling operations (working losses) and from breathing losses associated with thermal expansion, pressure fluctuations and continuous vaporization.

General formulas[9] for estimating both working and breathing losses have been developed by the American Petroleum Institute. In general, the breathing losses are one to two orders of magnitude less than working losses and will not be considered here.

The working loss rate is given by:

$$W = 1000\ D\ m\ P\left(\frac{180 + N}{6N}\right)$$

where W = working loss in $\text{lb}/10^3$ gal throughput
D = oil density in lb/gal
m = empirical factor estimated to be 1.5×10^{-4} for residual oil
P = vapor pressure at the bulk oil temperature
N = number of tank refills per year.

For the demonstration plant, the following values are assumed: $D = 8.1$ lb/gal; $P = 4.6$ psia; $N = 126$ refills/year based on continuous operation. Thus $W = 2.3\ \text{lb}/10^3$ gallon throughput or 230 lb vapor/tank refill (104 kg vapor/tank refill).

For the commercial system the short term tank will hold a 2-day oil supply and will be refilled every 24 hours during one 8-hour shift. Thus D and P are the same as above but $N = 182.5$. The working loss W becomes $1.85\ \text{lb}/10^3$ gallon throughput or 827 lb vapor/fillup (376 kg/fillup). Assuming this working loss is distributed evenly over the 8-hour shift, the fugitive oil emission rate is equal to 13 kg/s (103 lb/hr). This emission rate for the short term tank is equally applicable to fillup from either rail car or from the long term tank.

Similar considerations apply to kerosene tanks and the long-term tank in the 250 MW unit. However, these tanks will be filled up infrequently. In Section V, the chemical nature of fugitive emissions from bitumen storage and handling are discussed in more detail.

FUGITIVE AIR EMISSIONS FROM RESOX^{TM} COAL STORAGE AND HANDLING

At the demonstration plant crushed coal will be delivered by truck and stored in a silo. Coal will be transferred by a vibrating feeder and bucket elevator to a feed bin directly over the reactor. The only information available regarding RESOX^{TM} coal handling for the 250 MW unit is that front-end loaders will transport coal from the stock pile to the reactor.

Particulate emissions from coal piles are influenced by wind speed, pile surface area, coal density, and the prevailing precipitation - evaporation index. The dust emission factor from coal piles is estimated to be equal to 0.59 mg/kg-yr (0.00118 lb/ton-yr).[8] Wind erosion from stationary coal piles represents only 1/3 of total particulate emissions from coal storage and handling;[8] therefore this factor is multiplied by 3 to derive the total emission rate from coal storage, conveying, and feeding.

The annual RESOX^{TM} coal throughput at the demonstration plant will be approximately 1.2×10^6 kg (1.3×10^3 tons) and 1.6×10^7 kg (1.8×10^4 tons) at the 250 MW unit. Using these values in conjunction with the emission factor given above, uncontrolled fugitive dust emission rates from RESOX^{TM} coal will be 6.7×10^{-2} mg/s (5.3×10^{-4} lb/hr) at the demonstration plant and 0.89 mg/s (7.1×10^{-3} lb/hr) at the commercial facility.

FUGITIVE AIR EMISSIONS FROM LIMESTONE STORAGE AND HANDLING

FW Demonstration Plant

At the demonstration plant fugitive limestone dust will be released by storage and transport operations. Emission rates for these unit operations are difficult to estimate but calculations based upon published[9] empirical rates for rock handling processes may be appropriate. Total uncontrolled emission rates due to screening, conveying and handling are estimated to be 5 g/kg (10 lb/ton). Although no figures are given for the percentage of this total which falls into the suspended particulate range, approximately 50 percent of the uncontrolled losses from rock crushing settle out in the immediate vicinity of that operation. Applying this 50 percent factor to the above emission rate sets this at 2.5 g/kg (5 lb/ton). In addition, Foster-Wheeler plans to incorporate a filter over the limestone surge bin. This control device would remove approximately 99 percent of the fugitive dust,[9] lowering the controlled emission rate to 25 mg/kg (0.05 lb/ton). Applying this factor to the limestone feed rate of 0.123 kg/s (975 lb/hr) yields an emission rate of 3 mg/s (0.024 lb/hr). Additional fugitive dust emissions from limestone storage should be negligible by comparison. There is no drying unit designed for the 10 MW Demo and, therefore, no related fugitive emissions.

FW 250 MW Unit

The proposed design for the 250 MW commercial unit calls for crushing and drying of limestone in addition to handling and storage. Estimates of emission factors for these operations can be obtained from AP-42[9] factors for lime manufacturing. This publication indicates that primary and secondary crushing operations generate particulate emissions of 15.5 g/kg (31 lb/ton) and 1 g/kg (2 lb/ton) respectively. Because the analyses presented here reflect worst case situations, it will be assumed that the factor for primary crushing is applicable. The preliminary FW design does not include a baghouse over the crushing unit although such a control device is indicated as an adjunct to the dryer. A baghouse filter would reduce crushing emissions by 99 percent to 0.16 g/kg (0.31 lb/ton). Therefore, at a limestone feed rate of 1.6 kg/s (12,600 lb/hr) a worst case analysis predicts uncontrolled crushing emissions will be 25 g/s (200 lb/hr) and controlled emissions will be 0.25 g/s (2 lb/hr).

No specific data are available regarding air emissions from limestone drying. For a worst case analysis comparative emissions expected from calcining operations may be illustrative of the order of magnitude involved. The emission factor given by AP-42[9] for rotary kiln calcining is 100 g/kg (200 lb/ton). With use of a baghouse filter, as proposed by FW for the 250 MW unit these emissions will be reduced by about 99 percent to 1 g/kg (2 lb/ton). At a feed rate of 1.6 kg/s (12,600 lb/hr) a worst case analysis of limestone drying predicts an emission rate of 1.6 g/s (12.6 lb/hr).

Additional emissions due to limestone screening, conveying and handling if unabated by a control system would be roughly 4 g/s (31.5 lb/hr) or 0.04 g/s (0.32 lb/hr) if covered by a baghouse unit. This is estimated from applying the emission factor derived for the 10 MW Demo to the limestone feed rate stipulated for the 250 MW plant.

Therefore, total fugitive air emissions at the 250 MW unit resulting from limestone storage, handling and drying operations will fall in the range of 1.9 g/s (13 lb/hr) to 30.6 g/s (244 lb/hr).

TRACE ELEMENT EMISSIONS

Trace element emissions from the fuel oil combustion can present environmental impacts by several pathways:

- Enrichment - Toxic elements (e.g., Pb, V) can volatize and selectively condense on small particulates in the combustion process. These enriched fine particulates are doubly problematical in that they are difficult to control at the stack exit and once released, they can readily penetrate deeply into the lung.

- Vaporization - Some toxic compounds are sufficiently volatile to be emitted from the combustor in the gas phase (e.g., Hg, F, Se).

- Formation of carcinogenic compounds - Compounds of certain trace elements (Cr, Ni) are carcinogenic. These emissions are of particular concern because quantitative correlations between ambient concentrations of these species and health effects have not been established.

The unique feature of the CAFB limiting trace element emissions is that the limestone bed acts as a sink for these species (e.g., V, Ni, and Fe).[2] In this fashion the gasifier itself functions as a control device for trace element emissions.

There are very few analyses available of the trace element content of limestone and residual oil or bitumen. The trace element content of residual oil may vary greatly depending on its origin. The analyses presented in Tables 4 and 5 for trace element composition of residual oil and limestone will be used for the estimates calculated here. Table 8 lists those elements found in oil or stone which are either volatile or toxic.

Table 8. VOLATILE OR TOXIC TRACE ELEMENTS IN OIL AND STONE

Cadmium	Vanadium
Cobalt	Zinc
Arsenic	Antimony
Lead	Chromium
Scandium	Copper
Tellurium	Fluorine
Iron	Nickel

The major source of trace element emissions through the stack is feed oil rather than limestone for two reasons:

- The oil/limestone feed ratio is greater than 10 to 1. Of the trace elements listed in Table 8 only iron is an order of magnitude more abundant in limestone than in oil.
- Trace elements in the sorbent are contained in a limestone matrix as the fairly unreactive oxide or carbonate (see Table 6); thus they will have much lower emission factors than the more volatile forms of trace elements (such as sulfides) encountered on the fuel.

To determine possible environmental impacts of trace element emissions a worst case analysis can be made, assuming that all trace elements in the fuel feed exit through the stack. If these emission rates can be shown to produce negligible environmental impacts, then trace element emissions will not be of concern in the CAFB.

Emission factors at the top of the stack for those elements called out in Table 8 are tested in Table 9. It has been estimated[10] that ground level ambient concentrations in the vicinity of the stack are on the order of 0.1 percent of those at the top of the stack. These ground level values are also listed in Table 9. To judge the potential environmental impact of these trace element emissions these ambient loadings should be compared with maximum acceptable ambient air concentrations or Multi-Media Environmental Goals (MEGS) established by EPA.[11] These factors are determined from Threhold Limit Values (TLV's)[12] set by OSHA by the following formula.

$$MEG = (8/24)(0.01)\ TLV$$

The factor 8/24 adjusts the 8-hour workday OSHA standard to 24-hour exposure, and the factor 0.01 provides a margin of safety for those people who are less healthy than the average industrial worker. Both TLV's and MEGS are listed in Table 9. For a given element to be of potential concern its ambient concentration must exceed its MEG.

Applying this criterion, vanadium, cadmium and nickel are the only trace elements whose worst case emission rates may be of concern. Previous ERCA studies, however, have shown that almost all fuel vanadium and three-quarters of the nickel are picked up by the gasifier bed material. In the ERCA analysis of fuel oil (Table 4) cadmium could not be distinguished from indium. Thus it is not at all clear that cadmium is present in the oil to any significant extent. Although the worst case analyses make no assumption about the physical form of trace elements exiting the stack, most of these elements will in fact condense on particulate surfaces as

Table 9. COMPARISON OF WORST CASE EMISSION ESTIMATES WITH AIR QUALITY GOALS

Element	Concentration at top of stack, mg/m^3	Ambient concentration, µg/m^3	TLV mg/m^3	MEG µg/m^3
As	0.19	0.19	0.5	1.7
Cd	0.45	0.45	0.05	0.17
Co	0.013	0.013	0.1	0.33
Cr	0.090	0.090	1.0	3.3
Cu	0.025	0.025	1.0	3.3
F	0.014	0.014	2.0	6.7
Fe	2.0	2.0	1.5	5.0
Ni	2.62	2.62	1.0	3.3
Pb	0.23	0.23	0.15	0.5
Sb	0.047	0.047	0.5	1.7
Te	0.064	0.064	0.1	0.33
V	19.65	19.65	0.5	1.7
Zn	0.17	0.17	5.0	16.7

the stack gas cools. Particulate chemical composition is discussed in detail in Section V.

WATER EMISSIONS FROM RESOX^{TM} COAL STORAGE

Surface run-off from natural precipitation constitutes the primary source of potential contamination of surface waters due to coal storage. The pollution potential of coal pile runoff depends upon local precipitation, pile area, storage foundation material and storage pile coating. Coal pile runoff usually has a low pH and a high concentration of dissolved solids including iron, magnesium, and sulfate. Aluminum, sodium, manganese, and other metals may also be present in undesirable amounts. Coal pile drainage contains dissolved metallic salts in the concentration range shown in Table 10. The variability of drainage composition reflects the

Table 10. COMPOSITION OF DRAINAGE FROM COAL PILES[13]

	Concentration, mg/l[a]
Alkalinity	15 - 80
BOD	3 - 10
COD	100 - 1,000
Total solids	1,500 - 45,000
Total suspended solids	20 - 3,300
Total dissolved solids	700 - 44,000
Ammonia	0.4 - 1.8
Nitrate	0.3 - 2.3
Phosphorus	0.2 - 1.2
Turbidity	6 - 505
Acidity	10 - 27,800
Total hardness	130 - 1,850
Sulfate	130 - 20,000
Chloride	20 - 480
Aluminum	825 - 1,200
Chromium	0 - 16
Copper	1.6 - 3.9
Iron	0.4 - 2.0
Magnesium	90 - 180
Sodium	160 - 1,260
pH	2.2 - 8.0

[a] Appropriate for all values except pH.

variety of coals used as well as the rate of rainfall. No specific data was found for anthracite, the type of coal to be used for the RESOX^{TM} at the demonstration plant. During heavy rainfall the level of dissolved solids in the runoff will be high initially and will rapidly decrease. When rainfall is light, the long retention time may allow more diffusion, and hence more chemical reaction to occur and result in higher pollutant concentrations. Meteorological conditions in the San Benito area produce relatively brief periods of heavy rainfall during the late summer and early fall and little other precipitation.

Accurate assessment of the runoff associated with the 250 MW unit must await site selection and specifics of the coal storage pile. An order of magnitude estimate of this emission can be made from general correlation data.[13] Assuming a 30-day supply of coal is kept on hand, the storage pile will hold up to 1.4 x 10^6 kg (3 x 10^6 lb). This corresponds to a volume of roughly 850 m^3 (3 x $10^4 ft^3$) which will be assumed to be contained in a pile of area 186 m^2 (2,000 ft^2) and height 4.6 m (15 ft). At an annual rainfall of 114 cm (45 in.) the yearly runoff would be 212 m^3 (7500 ft^3).

EMISSIONS FROM RESOX^{TM} SOLID WASTE

Spent fuel effluent from the RESOX^{TM} system amounts to 0.02 kg/s (150 lb/hr) at the demonstration plant and 0.25 kg/s (2,000 lb/hr) at the 250 MW unit. Foster Wheeler plans to market this material which is approximately 75 percent carbon and 25 percent ash as a low sulfur solid fuel with a heating value of about 5800 kcal/kg (10,500 Btu/lb). If this material is not marketable a number of disposal possibilities including ponding and landfill will have to be considered. Air, water and leachate emissions from these options should be carefully evaluated if such disposal will be required.

The other solid product from the RESOX^{TM} unit operations is sulfur. Foster Wheeler also plans to market this material. Nevertheless, sulfur processing and handling operations must be evaluated for their environmental impacts.

EMISSIONS ASSOCIATED WITH SPENT REGENERATOR STONE

Solid waste will be emitted from the regenerator in both Foster Wheeler designs and will be transported to the spent solids handling system where the solids will be cooled with air and pneumatically transported to a spent solids storage silo. The cooler air exhaust is vented to a cyclone and collected solids are sent to the storage silo. To reduce air emissions, the storage silo exhaust will pass through vent filters.

Foster Wheeler has considered the prospect of marketing the spent solid material. If marketing is not possible, the waste material must be disposed of in an environmentally acceptable manner. As is the case with sulfur, unit operations associated with marketing must be carried out in an environmentally acceptable manner.

Spent stone from the CAFB cannot be disposed of as a solid landfill in an environmentally acceptable manner without further treatment. The stone consists of from 3 to 5 percent CaS which will react with moisture in the air to liberate H_2S. The H_2S will be oxidized in the atmosphere to SO_2. This SO_2 will add to the SO_2 emissions from the CAFB unit and the whole system could exceed federal SO_2 standards. For example, Westinghouse has determined that if 90 percent of the fuel sulfur is retained in the bed and 70 percent of the waste sulfide is converted to sulfate, then the total emissions from the CAFB and waste disposal pile would exceed the current federal SO_2 emission standard (0.8 lbs $SO_2/10^6$ Btu) after 12 years assuming a 6 percent sulfur annual loss rate.[3] Clearly, the waste stone must be treated to remove the sulfide or render it inert.

Westinghouse[4] has been investigating several methods for spent stone processing prior to disposal. These methods include:

- Dry sulfation - reacting stone with SO_2 and O_2 at 870°C (1600°F) to produce a product containing 90 percent $CaSO_4$ and 10 percent CaO.
- Missing stone with coal fly ash and hot pressing.
- Wet slurrying with carbonation - reacting spent lime with water and CO_2 to produce $CaCO_3$ and H_2S.

Three possible disposal options are also being considered: sale of processed stone, land filling and ocean dumping. As yet no combination of processing and disposal has been shown to be environmentally acceptable.

EMISSIONS AND ENVIRONMENTAL EFFECTS OF CONDENSER COOLING

The La Palma power station condensers are cooled by six mechanical draft cooling towers.[14] These cooling towers are visible in Figure 7 which is an aerial photograph of the power plant. The FPC Form 67 data stipulates a cooling water recirculation rate of 10.8 m^3/s (380 ft^3/s) in order to service the entire 230 MW of plant capacity.[14] The use of the 10 MW CAFB demonstration plant should have negligible effect on the overall quantity and characteristics of cooling water withdrawal, recirculation, and discharge. A summary of potential environmental impacts produced by the La Palma cooling towers are presented in Table 11.[15]

Thermal Discharge

Makeup water is required at a rate of 0.09 m^3/s (3.15 ft^3/s) and discharged at 0.025 m^3/s (0.9 ft^3/s), reflecting an evaporative water loss of 0.06 m^3/s (2.25 ft^3/s).[14] The cooling water experiences a temperature rise of 9°C (16°F) as it circulates past the condensers. Thermal discharge to the water environment will depend upon whether blowdown is performed at the cold side or hot side of the cooling system. If blowdown is done on the hot side, a conservative estimate of heat rejection to the ambient water is 10 percent of the heat content of the recirculating cooling water.[13] At

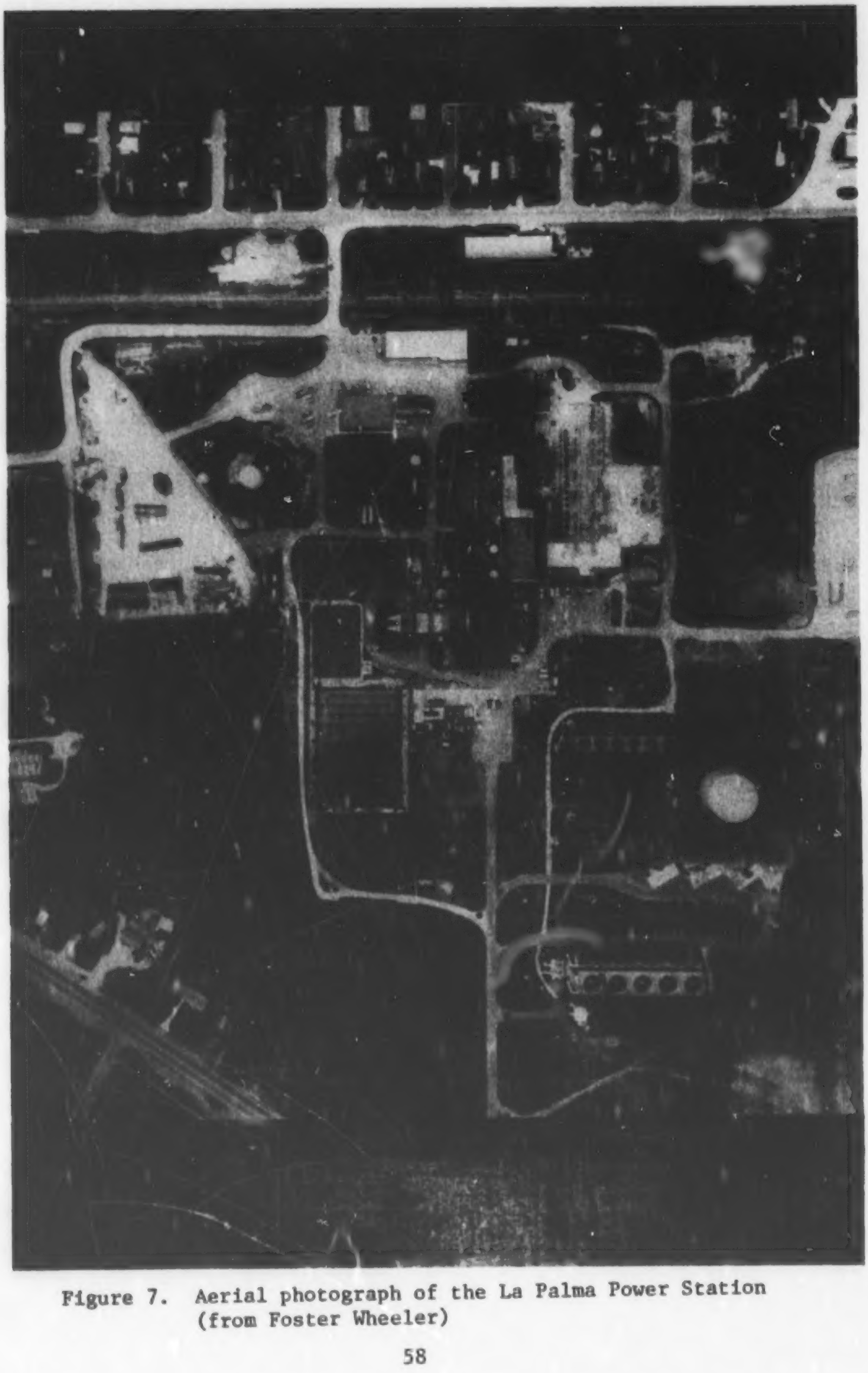

Figure 7. Aerial photograph of the La Palma Power Station (from Foster Wheeler)

Table 11. SUMMARY OF POTENTIAL ENVIRONMENTAL IMPACTS FROM THE LA PALMA STATION COOLING TOWERS[15]

Atmospheric effects	Hydrologic and aquatic effects	Other effects
Visible plume: visual obstruction, ground shading, and reduction in visibility to various modes of transportation.	Blowdown: potential increase of water temperature near discharge point, contamination of surface-water and groundwater supplies, potential increase of soil salinity.	Land use: large land areas required for each of the cooling systems.
Ground fog: potential hazard to land and water transportation and nuisance to nearby communities.	Water consumption: potential depletion of surface-water and groundwater resources.	Sound levels: nuisance to nearby residents and transient observers.
Icing: hazard to land transportation and ice accumulation on nearby structures and utility wires.	Seepage and leakage water: same effects as blowdown discharges.	Aesthetics: unsightly to nearby residents and transient observers.
Drift deposition: potential damage to biota, acceleration of corrosion of nearby structures, and contamination of soil and water bodies.	Intake screen devices: impingement or entrapment of aquatic life.	
Cloud formation: visual obstruction and potential local weather modifications.	Transport through condensers and circulation pumps: damage to aquatic organisms.	
Precipitation and snow augmentation: potential local weather modifications.	Discharge systems: disturbance to aquatic communities due to mechanical forces and turbulence.	

a ΔT of 9°C (16°F) and a discharge rate of 0.025 m^3/s (0.9 ft^3/s), the heat discharge to the ambient water is equal to 23 kcal/s (7.8×10^6 Btu/day).

The effect of heat discharge to ambient water is the reduction in the dissolved oxygen concentration, which can cause migration of aquatic species, fish kills, and a reduction in the capacity for natural stream purification.

Cooling Tower Blowdown Wastewater Discharge[16]

Federal regulations require that pollutants discharged in cooling tower blowdown will not exceed the concentrations noted in Table 12.

A recent EPA document[16] requires even more stringent limitations on effluent residual chlorine discharged into fresh water. Table 13 illustrates these specifications. The allowable residual chlorine concentration thus depends upon whether the cooling water is discharged to the tidal estuary portion of the Rio Grande or to the Gulf of Mexico.

As cooling water evaporates, all dissolved and suspended solids are concentrated in the cooling stream. The solubility of the constituents at specific temperature and pH limits the degree of concentration. Precipitation of solids onto metal surfaces can occur and is prevented by injecting chemical additives for control of scale, corrosion, and algae, slime, and fungi buildup. Tables 14[18] and 15[13] illustrate the type and concentration of chemicals mixed into cooling tower water.

The FPC Form 67 summary[14] for the San Benito Plant states that 3 tons/yr of chlorine are added to the circulating cooling water in order to control the fouling of metal surfaces with microorganism growth. Disregarding any chlorine reaction results in a residual chlorine discharge of 3.4 mg/l, which is an order of magnitude higher than the limits noted in Table 12. This is an extremely conservative estimate based solely on a worst case analysis and actual free chlorine discharge will be much lower than

Table 12. WATER EFFLUENT STANDARDS[16]

Pollutant	1-day maximum concentration, mg/l	30-day average concentration, mg/l
Free available chlorine	0.5	0.2
Zinc	1.0	1.0
Chromium	0.2	0.2
Phosphate	5.0	5.0
Other corrosion inhibiting materials	Limit to be established on a case by case basis	

Table 13. RESIDUAL CHLORINE RECOMMENDATIONS[17]

Type of chlorine use	Residual chlorine concentration, mg/l	Degree of protection
Continuous	<0.01	Protects trout and salmon and other important fish food organisms. Potentially lethal to more sensitive species.
	<0.002	Protects most aquatic organisms.
Intermittent — 2 hrs/day	<0.2	Protects trout and salmon.
	<0.04	Protects most aquatic organisms.

Table 14. CHEMICALS USED IN RECIRCULATIVE COOLING WATER SYSTEMS[18]

Use	Chemical
Corrosion inhibition or scale prevention in cooling towers	Organic phosphates Sodium phosphate Chromates Zinc salts Synthetic organics
Biocides in cooling towers	Chlorine Hydrochlorous acid Sodium hypochlorite Calcium hypochlorite Organic chromates Organic zinc compounds Chlorophenates Thiocyanates Organic sulfurs
pH control in cooling towers	Sulfuric acid Hydrochloric acid
Dispersing agents in cooling towers	Lignins Tannins Polyacrylonitrile Polyacrylamide Polyacrylic acids Polyacrylic acid salts
Biocides in condenser cooling water systems	Chlorine Hypochlorites Sodium pentachlorophenate

Table 15. COOLING TOWER CORROSION AND SCALE INHIBITOR SYSTEMS[13]

Inhibitor system	Concentration of chemical additives in recirculating water, mg/l
1. Chromate	200 - 500 mg/l $CrO_4^{=}$
2. Chromate + Zinc	17 - 65 mg/l $CrO_4^{=}$ 8 - 35 mg/l Zn^{++}
3. Chromate + Zinc + Phosphate (inorganic)	10 - 15 mg/l $CrO_4^{=}$ 8 - 35 mg/l Zn^{++} 30 - 45 mg/l $PO_4^{\equiv}$
4. Zinc + Phosphate (inorganic)	8 - 35 mg/l Zn^{++} 15 - 60 mg/l $PO_4^{\equiv}$
5. Phosphate (inorganic)	15 - 60 mg/l $PO_4^{\equiv}$
6. Phosphate (organic)	15 - 60 mg/l $PO_4^{\equiv}$ 3 - 10 mg/l organics
7. Organic biocide	30 mg/l chlorophenol 5 mg/l sulfone 1 mg/l thiocyanate

specified limits because most of the added chlorine will be chemically bound to other species contained in the cooling water.

Dissolved species in cooling water may be naturally occurring or introduced as corrosion inhibitors, biocides, pH controls, and dispersants. When the concentration of these ions exceeds solubility limits, salt will precipitate. The solubility of some salts decreases when the temperature rises. Salts exhibiting this characteristic are likely to precipitate and form scale on hot condenser tube walls and reduce heat transfer. The most common way to control scale formation is to blowdown a portion of the circulating water stream and replace it with fresh water so that the ion concentration in the circulating water does not reach saturation at any time. Blowdown (B) is a function of cooling water makeup quality. As shown below, the volume of cooling water makeup (M) required is equal to the sum of the volume of cooling water lost as blowdown (B), drift (D), evaporation (E), and seepage or leakage (S). S is very small in comparison to the other volume parameters and can be neglected without significantly affecting calculated volumes.

$$M = B + D + E + S$$

It follows that the volume of blowdown is a function of makeup water quality and can be determined from the following expression.

$$B = \frac{E - (S + D)(C - 1)}{C - 1}$$

where C = cycles of concentration (dimensionless).[13]

Cycles of concentration is the number of times that the solute species can be concentrated before one particular constituent concentration exceeds a critical level. C can be increased as influent water quality increases. This qualitatively illustrates the degree to which influent water quality can degrade prior to falling below acceptable levels. The equation shows that for a constant rate of evaporation, drift and seepage the required blowdown decreases as C increases. The equation represents a tradeoff between external feedwater treatment and internal chemical conditioning needs.

For average quality cooling water makeup, the value for C is conventionally kept between 4 and 6. For extremely high quality cooling water makeup, C values of 15 and above may be employed. When saline cooling water is used, C generally ranges between 1.2 and 1.5.[13]

Cooling Tower Drift

Warm moist air discharged from cooling towers contains water droplets which range in diameter from a few to several hundred micrometers. Those droplets greater than 20 μm in size are considered as drift and smaller droplets constitute fog. Whereas fog is relatively pure condensed water vapor, drift droplets contain the same concentration of dissolved chemicals as the circulating cooling water.[19,20]

Cooling tower characteristics which affect drift rates[19] include:

- Volume of circulating water in the system per unit time
- Tower features (height, diameter, and characteristics of drift eliminators for natural-draft tower; height, cell diameter, characteristics of drift eliminators, and number of cells for mechanical draft tower)
- Drift flux and droplet size distribution
- Exit temperature
- Efflux velocity

Smaller size water droplets remain in the cooling tower plume for longer time periods than larger heavier droplets. As the heavier droplets fall out they are affected by atmospheric turbulence. Atmospheric characteristics which affect drift deposition include:[19]

- Ambient temperature,
- Relative humidity,
- Atmospheric stability,
- Mixing layer depth,
- Wind speed and direction, and
- Precipitation.[18]

Cooling tower drift losses vary between 0.005 and 0.02 percent of the cooling tower circulation rate.[13] This amounts to 6 to 50 x 10^{-4} m^3/s (1.2 to 4.8 cfm) drift discharged to the atmosphere from the mechanical draft cooling towers in use at the La Palma Power Station.

Fogging

Plumes from cooling towers have the potential to produce conditions of fogging and icing. Normally the plume will mix with the ambient air and not inhibit visibility. However, during thermal inversions and periods of high humidity and low temperature, the plume can become bounded close to the ground surface and cause fogging. Fogging is generally limited to the cooling tower site (within ~600m (2000 feet) of the tower). The probability of occurrence is higher with mechanical draft than natural draft cooling towers.[17]

Water Consumption

The mechanical draft cooling towers in use at the La Palma station cool primarily by latent heat transfer; only about 25 percent of heat loss is through sensible heat transfer.[17] The FPC reports that 0.064 m^3/s (2.25 ft^3/s) of water is evaporated by the La Palma cooling towers.[14]

EMISSIONS FROM BOILER WATER TREATMENT AND BOILER BLOWDOWN

Boilers in steam-electric power plants require that makeup water be added to steam condensate return in order to compensate for recirculating water lost during boiler blowdown, steam soot blowing, venting, gland and boiler tube leakage. The required quantity and quality of feedwater is a function of boiler operating pressure and heat transfer rate. It is not anticipated that feedwater requirements and water emissions will change after the 10 MW CAFB is retrofitted to Unit No. 4 at the La Palma Power Plant.

The La Palma Plant uses fixed bed demineralizers for treatment of feedwater used in boiler units 4 and 6.[21] This is an ion exchange process in which undesirable ions such as calcium and magnesium react with a polymeric resin and are removed from the feedwater. Both positive and negative ions are removed by cation and anion exchange resins. Cation resins are generally synthetic polymeric materials containing ion groups such as SO_3H^-. Common anion exchange resins are synthetic amines.[22]

A typical cation exchange reaction is:

$$Ca^{++} + H_2 \cdot R \rightleftharpoons CaR + 2H^+$$

where R represents the cation exchange resin.

When the exchange resin's capacity for collecting more cations is exhausted, it is regenerated by passing a 2 to 10 percent H_2SO_4 solution through the bed; i.e.,

$$Ca \cdot R + 2H^+ \rightleftharpoons H_2 \cdot R + Ca^{++}$$

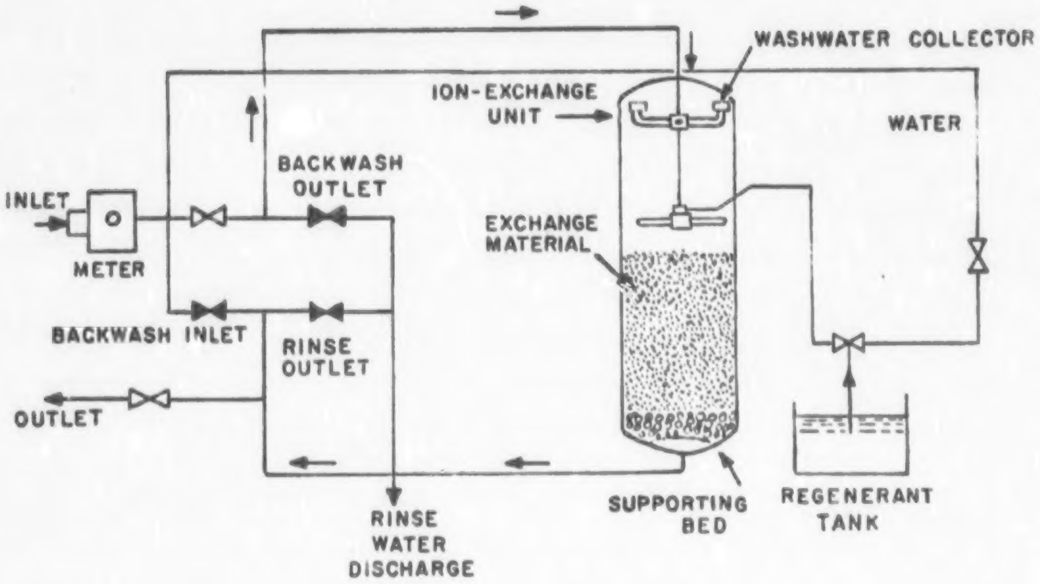
WASHWATER COLLECTOR
ION-EXCHANGE UNIT
WATER
BACKWASH OUTLET
INLET
METER
EXCHANGE MATERIAL
BACKWASH INLET
RINSE OUTLET
OUTLET
SUPPORTING BED
REGENERANT TANK
RINSE WATER DISCHARGE

Figure 8. Fixed bed ion exchange system[23]

Anion exchange replaces undesirable anions with hydroxide ions according to:

$$SO_4^{=} + R\cdot(OH)_2 \rightleftharpoons R\cdot SO_4 + 2OH^-$$

Regeneration is accomplished by passing 5 to 10 percent solution of sodium hydroxide through the bed:

$$R\cdot SO_4 + 2OH^- \rightleftharpoons R\cdot(OH)_2 + SO_4^{=}$$

Actual treatment involves a number of steps. The feedwater is passed through the resin bed until an excess of contaminant appears in the effluent. Following such breakthrough, the bed is backwashed and the resin regenerated and rinsed. The bed is then ready for another treatment cycle.[22] Figure 8 schematically illustrates in ion exchange treatment unit.[23]

Backwashing is performed after breakthrough for a period of about 10 minutes at a flow rate of 3.4 to 4.8 liters per second per square meter (5 to 7 gallons per minute per square foot) of bed area. This step removes any accumulated dirt and loosens the resin to prevent flow channeling during subsequent treatment cycles. After regeneration, excess regeneration solution and spent solution is rinsed from the bed. The total volume of rinse water required is approximately 3.34×10^3 liters per m^3 (25 gallons per ft^3) of bed volume. The waste materials carried in the rinse water are primarily sodium, calcium and magnesium chlorides or sulfates, plus excess sulfuric acid or alkali (NaOH) used for regeneration.[13]

Boiler Blowdown

In order to maintain dissolved and suspended solids below specified levels, a portion of the circulating boiler water is periodically or continuously discharged from the system. If solids are allowed to accumulate they will eventually precipitate onto heat transfer surfaces and cause efficiency and structural integrity to deteriorate.

Pollutants discharged with boiler blowdown include suspended and dissolved solids, hardness, phosphates, and alkalinity. Total dissolved solids content ranges between 10 and 100 mg/l. At La Palma, hydrazine is added to condensate return for corrosion prevention and it is estimated that blowdown pH ranges between 9.5 and 11 and contains ammonia at a concentration of 1 to 2 mg/l.[13]

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SECTION V

FIELD TEST PROGRAM AND LABORATORY RESULTS

INTRODUCTION

The field test program carried out by GCA at the ERCA CAFB pilot plant during the period November 24 to December 11, 1975, was directed primarily toward flue gas and particulate emissions and secondarily toward solid waste effluents. The goal of this effort was to characterize as completely as possible, within the economic and time constraints of the project, the physical and chemical properties of the emissions from the boiler stack. Specific details of the field test program evolved during the course of the testing, being largely dependent on the operating parameters of the pilot plant.

Coincident with the planning and pre-test site visit was the announcement of the "multilevel phased approach"[1] to source sampling and analysis by the Process Measurements Branch of IERL. Because this project is a preliminary environmental assessment of a facility which heretofore had not been subjected to a comprehensive emissions assessment a decision was made early on in the project to combine measurements of the "criteria pollutants" using the standard EPA methods with the Level 1 approach[1] to determination of organic and inorganic emissions. The rationale for this approach is that the CAFB demonstration plant and proposed commercial unit will have to meet local, state and federal emission standards and new source performance standards for particulate, NO_x, SO_x, and CO. Furthermore, because this study has as one of its goals the generation of recommendations for more comprehensive testing of the Foster-Wheeler demonstration plant currently being designed, that extensive Level 1 information for a number of operating conditions would be more valuable than detailed data on a limited number of specific pollutants.

The GCA field team collected flue gas samples during normal gasification of bitumen and fuel oil, as well as during startup and abnormal (clogged gasifier/regenerator stone transfer system) operation. Actual sampling was accomplished during seven different pilot plant runs. In addition to stack gas samples, the GCA team collected spent regenerator stone, leached stone, gasifier bed stone, cyclone fines and fuel and limestone feed samples for subsequent laboratory analysis.

The following subsections detail the sampling and analytical techniques employed in the field and in the laboratory, the pilot plant operating conditions and the results of the test program.

FIELD SAMPLING PROTOCOL

As shown schematically in Figure 8 flue gas leaves the boiler via a 68.6 cm (2.25 ft) diameter duct from which approximately 5 percent of the flow is diverted through an experimental baghouse. The remaining flue gas encounters a knockout baffle and cyclone and then exhausts through a 68.6 cm (2.25 ft) diameter stack. Three ports (labeled A in Figure 9) spaced 120 degrees apart are located approximately six diameters upstream from the flue gas entry into the stack. Figure 10 is a photograph of the stack showing the locations of the sampling ports, the cyclone and the knockout baffle. Two of the stack ports are 3-inch BSP and one is 2-inch BSP. Figure 11 is a closeup picture of two of the three ports. Installation of a fourth port to allow for perpendicular traversing would have weakened the structure.

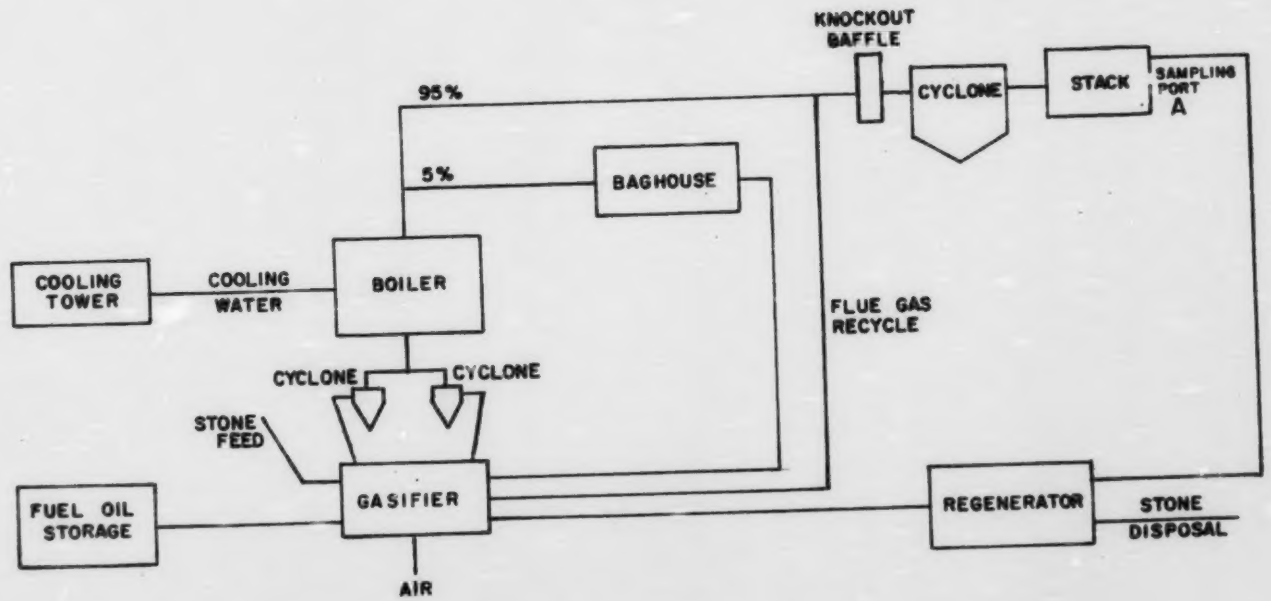
KNOCKOUT BAFFLE
95%
CYCLONE
STACK
SAMPLING PORT A
5%
BAGHOUSE
COOLING TOWER
COOLING WATER
BOILER
FLUE GAS RECYCLE
CYCLONE
CYCLONE
STONE FEED
GASIFIER
FUEL OIL STORAGE
REGENERATOR
STONE DISPOSAL
AIR

Figure 9. CAFB pilot plant

Figure 10. Pilot plant stack

Particulate sampling was accomplished using a standard RAC train constructed according to the procedures outlined in EPA Method 5.[2] Due to the positions of the installed ports, eight point traverses were taken on two diameters 120 degrees apart. The train was modified slightly to allow for sampling of gaseous organic species (see below).

Particulate size distribution measurements were taken with a University of Washington eight stage instack impactor using ungreased substrates. A single point was sampled isokinetically for sufficient time (15 to 30 minutes) to collect a weighable quantity on each stage.

In addition to particulate, flue gas was sampled for NO_x by Method 7,[2] SO_2/SO_3 by Method 8[2] and H_2S by Method 11.[2] An Orsat analyzer was used to measure CO, CO_2 and O_2.

To collect gaseous organic species the RAC train was modified by placing a gas adsorbent column between the filter and the impingers. This column, shown in Figure 12, was developed by Battelle Columbus Laboratories and made available to GCA for this program. Flue gas, after passing through the filter, is cooled to slightly above its dew point and then passes through a cell containing Tenax GC adsorber. This polymer reportedly collects all organic gases C_6 and above. After sampling for approximately 1 hour the adsorbent columns were capped and stored in darkness to await laboratory analysis.

Figure 11. Stack sampling ports

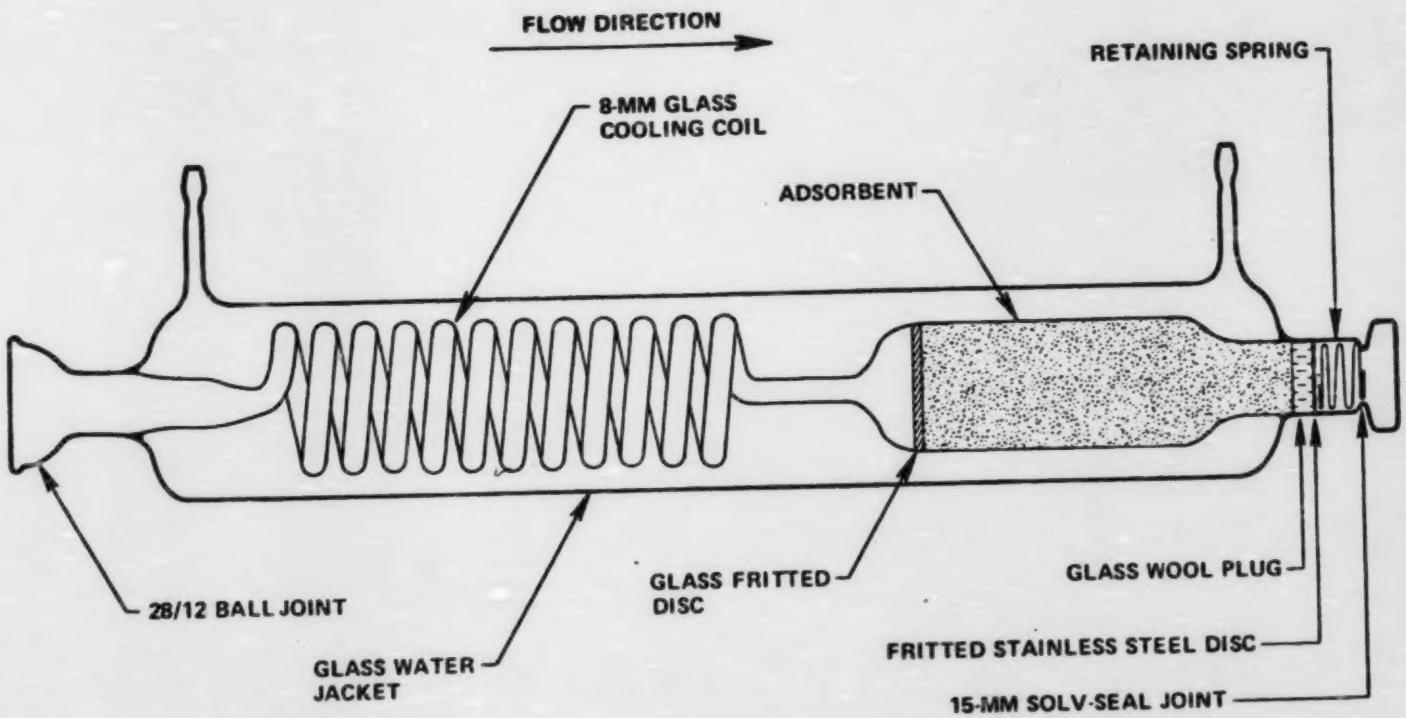
FLOW DIRECTION
RETAINING SPRING
8-MM GLASS COOLING COIL
ADSORBENT
28/12 BALL JOINT
GLASS WATER JACKET
GLASS FRITTED DISC
GLASS WOOL PLUG
FRITTED STAINLESS STEEL DISC
15-MM SOLV-SEAL JOINT

Figure 12. Absorbent sampling system

FIELD ANALYSES

Analyses for total particulate, SO_2/SO_3, NO_x, H_2S and particle size distribution were performed on-site in ERCA laboratories by GCA personnel. The procedures outlined in EPA Methods 5, 7, 8 and 11 were followed for the analyses of total particulate, NO_x, SO_x and H_2S, respectively. To preclude degradation, all standards, except barium perchlorate and potassium dichromate which are stable for long periods of time, were prepared at ERCA.

LABORATORY ANALYSES

Three general types of analytical procedures were applied to oil, flue gas, particulate and solid waste samples collected during the field test program: organic functional group identification; trace element quantification; and surface element and inorganic compound quantification. Organic functional group and trace element analyses were performed according to the procedures outlined in the EPA Level 1 protocol;[1] surface analysis is more properly a Level 2 technique. Each analytical technique is described below.

Organic Functional Group Analysis*

In this procedure,[3] sample extracts are separated into eight fractions by liquid chromatography (LC), evaporated to dryness, weighed, redissolved and analyzed by infrared spectroscopy. Methylene chloride was used to extract oil, particulate and spent stone samples; pentane was used to extract organic vapors adsorbed on the Tenax polymer.

Liquid chromatographic separation into eight fractions is accomplished by transferring the extract to an LC column and eluting sequentially with the following solvent mixtures:

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*These analyses were performed by Battelle Columbus Laboratories under subcontract and by the Process Measurements Branch of EPA.

(1) 25 ml 60/80 petroleum ether
(2) 25 ml 20% methylene chloride in 60/80 petroleum ether
(3) 25 ml 50% methylene chloride in 60/80 petroleum ether
(4) 25 ml methylene chloride
(5) 25 ml 5% methyl alcohol in methylene chloride
(6) 25 ml 20% methyl alcohol in methylene chloride
(7) 25 ml 50% methyl alcohol in methylene chloride
(8) 25 ml methyl alcohol.

Table 16 indicates the classes of organic compounds eluting in each fraction and their detection limits based upon the total sample extract. After collection from the LC column each fraction is reduced to dryness using a Kuderna-Danish evaporator and air evaporation and then weighed to determine the amount of organic material in each fraction.

The dried fractions are then redissolved in methylene chloride and subjected to IR analysis. The IR spectra are then scanned for functional group peaks.

Trace Element Analysis*

Stack particulate, spent stone, fuel oil, gasifier bed stone, gasifier cyclone fines, and knockout baffle material were analyzed for elemental composition using low precision (± 200 percent) spark source mass spectrometry (SSMS). This technique is sensitive to 70 elements. To calibrate the SSMS results, some elements were quantified by higher precision atomic absorption (AA) spectroscopy. Interference of organic ions with low atomic weight elements is well known in SSMS as are losses of volatile compounds. Thus uncertainties of values derived for light elements such as fluorine, sodium and sulfur may be higher than the indicated precision.

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*This work was performed by Battelle Columbus Laboratories and Aculabs under subcontract to GCA and by Northrup Services under contract to EPA.

Table 16. CLASSES OF ORGANIC COMPOUNDS ELUTING IN EACH LIQUID CHROMATOGRAPHY FRACTION, AND THEIR APPROXIMATE IR DETECTION LIMITS

Fraction	Compound type	Approximate IR sensitivity
1	Aliphatic hydrocarbons	1-10 μg
2	Aromatic hydrocarbons POM PCB Halides	1-10 μg
3	Esters Ethers Nitro compounds Epoxides	0.1-1 μg
4	Phenols Esters Ketones Aldehydes Phthalates	0.1-1 μg
5	Phenols Alcohols Phthalates Amines	0.1-1 μg
6	Amides Sulfonates Aliphatic acids Carboxylic acid salts	0.1-1 μg
7	Sulfonates Sulfoxides Sulfonic acids	0.1-1 μg
8	Sulfonic acids	0.1-1 μg

Surface Analysis

A number of particulate and solid samples were investigated for surface elements and inorganic compounds using X-ray photoelectron spectroscopy (XPS) also known as electron spectroscopy for chemical analysis (ESCA). In ESCA a high energy X-ray beam (for the analyses reported here the MgKα line having an energy of 1253.6eV was used) impinges on a solid knocking out core electrons from atoms on the solid surface. The resulting electrons pass through an energy analyzer and are pulse counted by a particle multiplier. The binding energy of the electrons is then calculated from the energy of the incident X-ray, the spectrometer work function and the measured electron kinetic energy. Binding energy ranges can be uniquely associated with specific precursor elements. In fact, ESCA is sensitive to all elements in the periodic table. An additional feature of ESCA spectra is that the precise electron binding energy in a known range is a function of the valence state of the atom of interest. For example, sulfur combined as sulfate can be differentiated from sulfur as sulfide. In addition, because core electron ejection cross sections are relatively independent of valence state, the ratio of the areas under the peaks corresponding to sulfate and sulfide is a measure of the sulfate-sulfide surface concentration ratio.

A further consequence of the independence of cross section upon valence state is that the relative concentrations of all elements on a surface can be calculated from known sensitivity values. Table 17 lists sensitivity factors applicable to the GCA/McPherson ESCA 36 instrument calculated from published photoionization cross sections.[4]

All samples analyzed by ESCA in this study were first scanned over the entire electron binding energy range (broadband scan) to identify those elements present in concentrations greater than 0.1 to 1 percent (the sensitivity of ESCA to any one element is a function of the photoionization cross section of the most intense core electron emission of that element).

Table 17. ELEMENTAL SENSITIVITY FACTORS FOR THE ESCA[36]

Element	Electron	Sensitivity factor
O	1s	430.8
	2s	36.6
C	1s	241
N	1s	340
K	2s	436
	2p	956
S	2p	496.8
Fe	2p	618.7
	3p	381
F	1s	562
Ca	2p	1215
Cl	2s	275
	2p	567
Si	2s	394.2
	2p	596
Pb	$4d_{5/2}$	459.8
	4f	4317 (±20%)
Al	2s	226
	2p	258.5
Sb	$3d_{3/2}$	3787
	4p	154.6
	4d	1331 (±25%)
As	3p	364
	3d	540
Na	2s	283.7
	2p	170.2
	KLL	1381
Cu	2p	589
	LMM	1060
Sn	3d	2990 (±25%)
P	2s	243.6
	2p	479.9
V	$2p_{3/2}$	1026.3
Mg	2s	220
	2p	167.4
Cr	2p	743.6
Cd	3d	2820.7

These broadband spectra were then analyzed to yield surface concentrations of all identifiable elements.

Some of the filter samples and impactor substrate samples had relatively light covering thus exposing portions of filter and aluminium foil to the X-ray beam. ESCA scans of these bare materials are shown in Figures 13 and 14.

The compound forms of surface vanadium and sulfur are also of interest in this study. They were investigated by scanning the binding energy ranges corresponding to the ejection of the 2p electron of vanadium and the 2p electron of sulfur. Figures 15 and 16 show the spectra of V_2O_5 and vanadium metal used as standards to bound the vanadium valence range between +5 and 0. The asymmetric bimodal structure of each spectrum is due to the presence of two spin-orbit states, $2p_{3/2}$ and $2p_{1/2}$, and not to two different oxidation states. In all vanadium analyses the position of the larger $2p_{3/2}$ peak was used as the comparison position. The oxygen ion peak, present in all vanadium scans, was used to calibrate the binding energy scale. Similarly, sulfate and sulfide bound the sulfur valence state scale between +6 and -2.

In addition to the vanadium and sulfur scans, the 1s peak of carbon was scanned over the energy range between 275 and 295 eV. This scan serves two purposes: the position of the carbon 1s peak at 284.8eV corresponding to hydrocarbons (the major carbon peak) calibrates the energy scale; and the size of the carbonate peak at 289.1eV indicates the surface concentration of this species relative to organic carbon species. In addition, the shape of the main carbon peak is indicative of hetero-atom substitution of the hydrocarbon species. Figure 17 displays the binding energies of carbon 1s electrons ejected from various carbon compounds.

To supplement the bulk SSMS analyses, high energy argon ions were used to etch away surface layers exposing strata 20 to 100 Å deep. The exposed sample layers were then rescanned over the entire binding energy range and

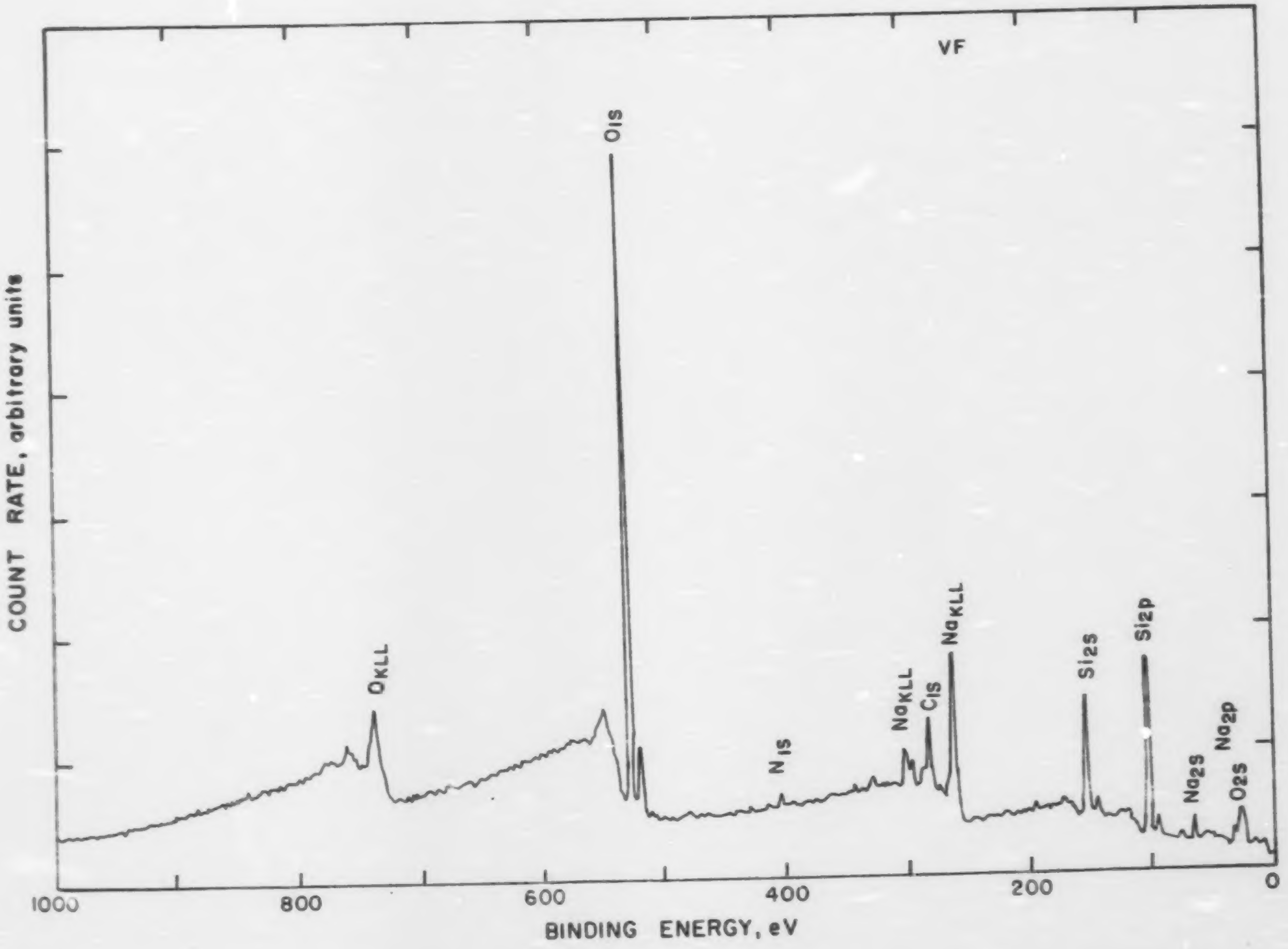

Figure 13. Hi-vol filter. Broadband ESCA scan

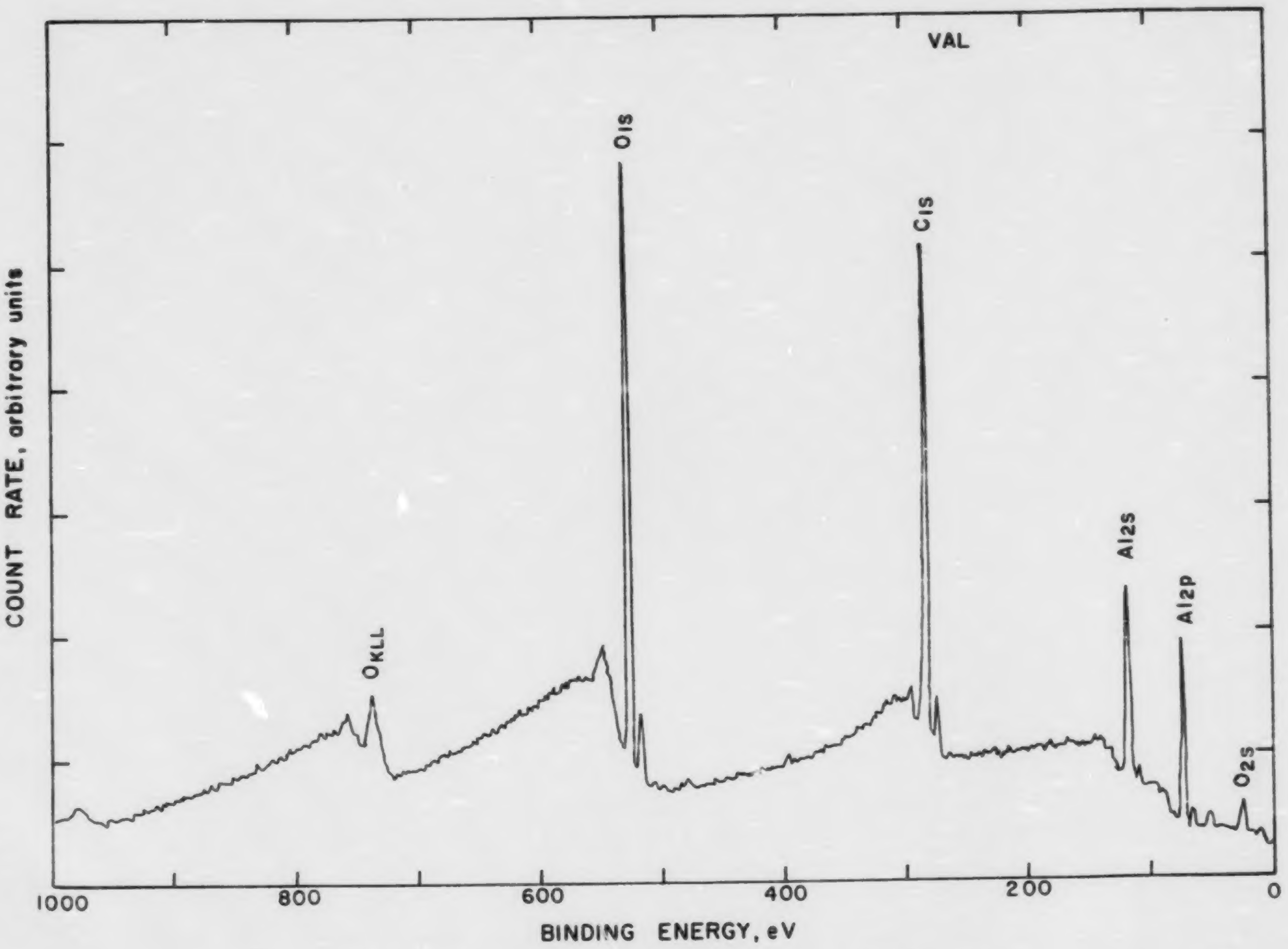

Figure 14. Aluminum substrate. Broadband ESCA scan

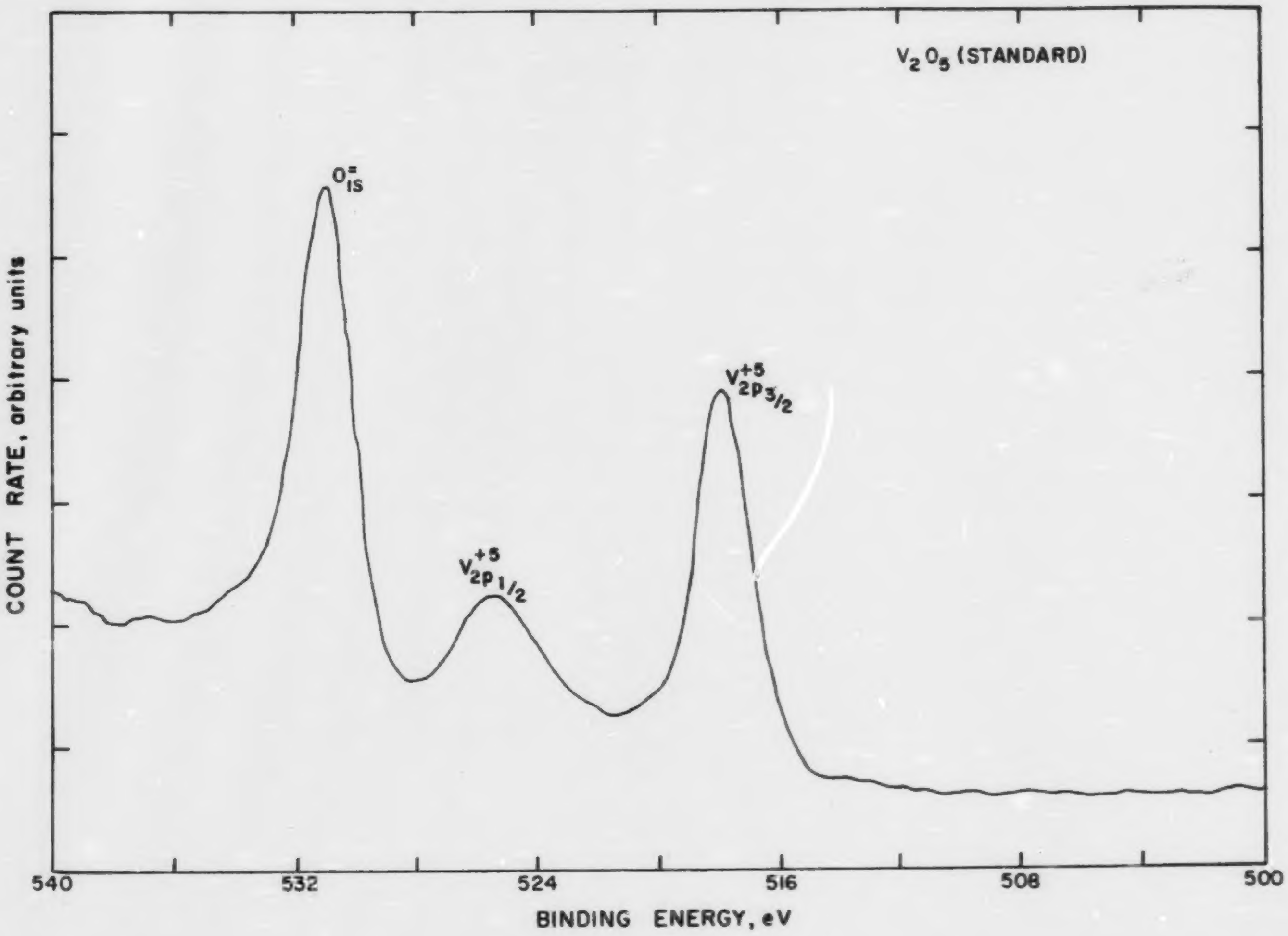

Figure 15. Vanadium metal ESCA scan

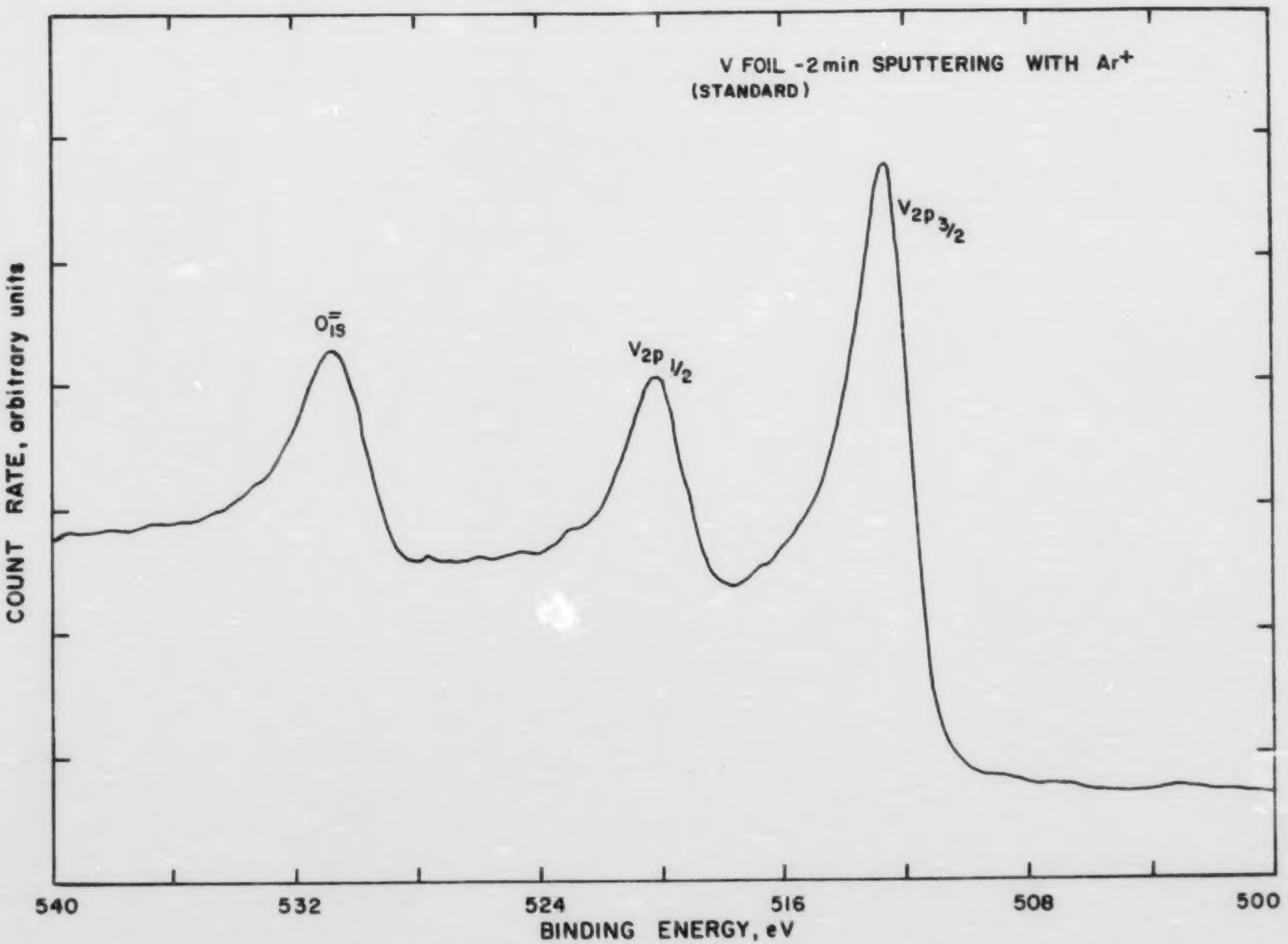

Figure 16. Vanadium pentoxide ESCA scan

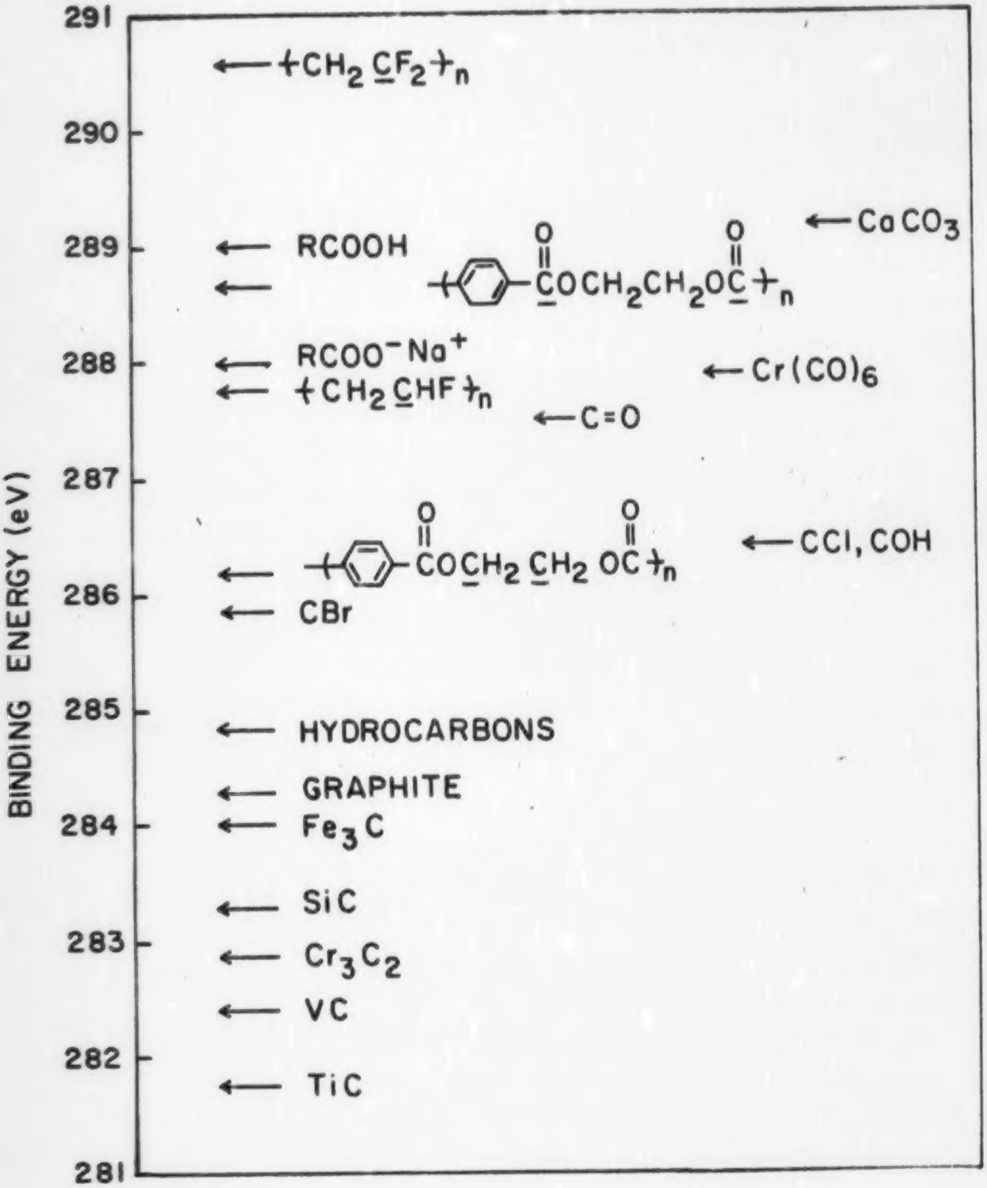

Figure 17. Carbon 1s binding energies

the resultant elemental concentrations were compared with the surface values and the SSMS analyses.

FIELD TEST PROGRAM

Stack sampling was carried out during three distinct operating conditions of the pilot plant: fuel oil gasification; bitumen gasification; bitumen combustion (startup). In all, seven sampling runs were made, four during fuel oil gasification, two during bitumen gasification and one during bitumen combustion. The number and duration of the tests were limited by pilot plant up time. Fuel oil gasification runs (Runs 1 to 4) approached "normal" operation; however, frequent cyclone malfunction occurred, resulting in variable particulate emissions. The first bitumen gasification run (Run 5) was rendered "abnormal" by clogging of the gasifier-regenerator stone transfer system with consequent buildup of sulfided stone in the gasifier. Later during this same run the transfer system was purged and fresh stone addition commenced. Startup operation (Run 6) consisted of bitumen combustion accompanied by fresh stone feed. The final test run (Run 7) was carried out during bitumen gasification and fresh stone feeding.

Table 18 summarizes pilot plant operating modes for Runs 1 to 7. Fluctuations in operating conditions occurred during several of the runs. The row labeled "Stone feed" refers to continuous operation; because of blockages in the gasifier-regenerator transfer system, stone was added at the beginning of Runs 1 to 4 after which the continuous feed system was shut down. Table 19 lists representative operating temperatures for all runs acquired from pilot plant log sheets. A comprehensive listing of all operating temperatures, pressures and feed rates is not presented here but will be published in a forthcoming ERCA/EPA report.

Table 20 summarizes field tests and samples collected during the field trip. The first group of emissions were measured or collected at the stack sampling port. The bottom group except for leached stone were acquired from ERCA personnel and retained for laboratory analysis.

Table 18. SUMMARY OF CAFB PILOT PLANT OPERATING MODES DURING TEST PROGRAM

Run	Date	Fuel[a]	Fuel heat input[b]	Gasifier operating mode	Stone feed
1	12/04/75	No. 6 oil	2.16×10^4 kcal/s (5.13×10^6 Btu/hr)	Gasification	Off
2	12/05/75	No. 6 oil	2.16×10^4 kcal/s (5.13×10^6 Btu/hr)	Gasification	Off
3	12/06/75	No. 6 oil	2.16×10^4 kcal/s (5.13×10^6 Btu/hr)	Gasification	Off
4	12/08/75	No. 6 oil	2.16×10^4 kcal/s (5.13×10^6 Btu/hr)	Gasification	Off
5	12/09/75	Bitumen	2.38×10^4 kcal/s (5.66×10^6 Btu/hr)	Gasification	On
6	12/10/75	Bitumen	2.38×10^4 kcal/s (5.66×10^6 Btu/hr)	Combustion	On
7	12/11/75	Bitumen	2.38×10^4 kcal/s (5.66×10^6 Btu/hr)	Gasification	On

[a] Feed rate: 2.27 l/s (36 gal/hr).

[b] Based on fuel oil specific gravity of 0.958 and heating value of 9.94×10^3 kcal/kg (1.79×10^4 Btu/lb) and bitumen specific gravity of 1.0185 and heating value of 1.029×10^4 kcal/kg (1.853×10^4 Btu/lb).

Table 19. REPRESENTATIVE PILOT PLANT OPERATING TEMPERATURES[a]

Unit operation	Temperature, °C	(°F)
Gasifier	900	(1652)
Regenerator	950	(1742)
Bitumen feed	160	(320)
Oil feed	85	(185)
Gasifier air feed	150	(302)
Top of stack	110	(230)

[a] From pilot plant log sheets.

Table 20. SUMMARY OF SAMPLING ACTIVITY

	Run							
Type of sample or test	1	2	3	4	5	6	7	Other
SO_x	X	X			X			
NO_x	X	X			X			
H_2S	X	X	X					
Total particulate	X	X	X	X	X	X	X	
Particulate sizing			X		X			
O_2	X	X		X	X	X	X	
CO_2	X	X		X	X	X	X	
CO	X	X		X	X	X	X	
Moisture	X	X		X	X	X	X	
Organic stack gases			X	X		X	X	
Gasifier bed	X	X			X			
Regenerator bed		X	X	X	X			
Left-hand cyclone[a]		X	X	X				
Right-hand cyclone[a]					X			
Knockout baffle		X	X		X			
Stack cyclone			X	X	X			
Bitumen								X[b]
Fuel oil		X						
Limestone					X			X[b]
Leached stone								X

[a] These cyclones are located between the gasifier and boiler.

[b] Obtained during pre-sampling site survey September 1975

The leached stone material is spent regenerator stone from a 1974 pilot plant run which was sintered and placed in leaching buckets on the ground near the plant. Six leached stone samples identified in Table 21 were collected.

Table 21. LEACHED STONE SAMPLES

Sample identification	Sintering temperature, °C	Sintering time, hours
SS1	1500	3
SS2	1500	1
SS3	1400	3
SS4	1400	1
SS5	1300	3
SS6	1300	1

FIELD TEST RESULTS

Tables 22 to 28 present the results of field analyses from Runs 1 to 7. Table 29 summarizes the emission measurements for SO_x, NO_x, H_2S and total particulate, each of which is discussed below.

$\underline{SO}_x$

Sulfur dioxide emissions during fuel oil gasification were approximately 0.65 $lb/10^6$ Btu (300 ppm), almost 20 percent below the New Source Performance Standard (NSPS) for oil-fired steam generators.[5] During these runs the SO_2 concentration in the regenerator off-gas ranged between 4 and 5 percent. This value is in good agreement with those reported by ERCA and with Foster-Wheeler projections of 0.64 and 0.78 $lb/10^6$ Btu for the demonstration plant and commercial CAFB unit, respectively.

Table 22. FIELD TEST RESULTS: RUN 1
FUEL OIL GASIFICATION

Emission or parameter	Rate or value		
Flue gas flow rate	0.56 dscm/s (1180 dscfm)		
Temperature at sampling port	108°C (226°F)		
Moisture	8.3 %		
CO_2	13.0 %		
O_2	1.0 %		
CO	0.1 %		
NO_x	0.102 g/dscm	(53.5 ppmv)	0.085 lb/10^6 Btu
SO_2	0.775 g/dscm	(292 ppmv)	0.643 lb/10^6 Btu
SO_3	0.027 g/dscm	(8.3 ppmv)	0.023 lb/10^6 Btu
H_2S	$<7 \times 10^{-5}$ g/dscm		
Total particulate	0.117 g/dscm		0.097 lb/10^6 Btu

Table 23. FIELD TEST RESULTS: RUN 2
FUEL OIL GASIFICATION

Emission or parameter	Rate or value		
Flue gas flow rate	0.51 dscm/s (1088 dscfm)		
Temperature at sampling port	109°C (229°F)		
Moisture	8.6 %		
CO_2	12.0 %		
O_2	3.8 %		
CO	0.1 %		
NO_x	0.087 g/dscm	(45.7 ppmv)	0.067 lb/10^6 Btu
SO_2	0.089 g/dscm	(305 ppmv)	0.619 lb/10^6 Btu
SO_3	0.026 g/dscm	(7.9 ppmv)	0.020 lb/10^6 Btu
H_2S	$<7 \times 10^{-5}$ g/dscm		
Total particulate	0.073 g/dscm		0.056 lb/10^6 Btu

Table 24. FIELD TEST RESULTS: RUN 3 FUEL OIL GASIFICATION

Emission or parameter	Rate or value
Flue gas flow rate	0.60 dscm/s (1265 dscfm)
Temperature at sampling port	111°C (231°F)
Moisture	9.7%
CO_2	12.2%
O_2	2.8%
CO	0.2%
H_2S	3.17×10^{-4} g/dscm (0.23 ppmv) 2.63×10^{-4} lb/10^6 Btu
Total particulate	0.080 g/dscm 0.067 lb/10^6 Btu

Table 25. FIELD TEST RESULTS: RUN 4 FUEL OIL GASIFICATION

Emission or parameter	Rate or value
Flue gas flow rate	0.58 dscm/s (1238 dscfm)
Temperature at sampling port	133°C (271°F)
Moisture	9.0%
CO_2	11.6%
O_2	5.3%
CO	0%
Total particulate	0.106 g/dscm 0.092 lb/10^6 Btu

Table 26. FIELD TEST RESULTS: RUN 5 BITUMEN GASIFICATION

Emission or parameter	Rate or value		
Flue gas flow rate	0.49 dscm/s (1040 dscfm)		
Temperature at sampling port	138°C (281°F)		
Moisture	9.5%		
CO_2	12.0%		
O_2	3.9%		
CO	0%		
NO_x	0.111 g/dscm	(58.4 ppmv)	0.079 lb/10^6 Btu
SO_2	2.194 g/dscm	(828 ppmv)	1.562 lb/10^6 Btu
SO_3	0.037 g/dscm	(11.1 ppmv)	0.026 lb/10^6 Btu
Total particulate	0.141 g/dscm		0.101 lb/10^6 Btu

Table 27. FIELD TEST RESULTS: RUN 6 BITUMEN COMBUSTION

Emission or parameter	Rate or value	
Flue gas flow rate	0.56 dscm/s (1193 dscfm)	
Temperature at sampling port	80°C (176°F)	
Moisture	2.4%	
CO_2	12.0%	
O_2	3.9%	
CO	0%	
Total particulate	0.056 g/dscm	0.104 lb/10^6 Btu

Table 28. FIELD TEST RESULTS: RUN 7 BITUMEN GASIFICATION

Emission or parameter	Rate or value	
Flue gas flow rate	0.51 dscm/s (1090 dscfm)	
Temperature at sampling port	127°C (261°F)	
Moisture	7.8%	
CO_2	12.0%	
O_2	3.9%	
CO	0%	
Total particulate	0.112 g/dscm	0.192 lb/10^6 Btu

Table 29. SUMMARY OF STACK EMISSIONS

Run	Fuel	NO_x		SO_2		SO_3		H_2S		Total particulate	
		ppm	lb/10^6 Btu	ppm	lb/10^6 Btu	ppm	lb/10^6 Btu	ppm	lb/10^6 Btu	ppm	lb/10^6 Btu
1	Fuel oil	53.5	0.0851	292	0.6431	8.3	0.023	<0.05			0.0971
2	Fuel oil	45.7	0.0671	305	0.6191	7.9	0.0201	<0.05			0.0561
3	Fuel oil							0.23	2.6×10^{-4}		0.063
4	Fuel oil										0.0921
5	Bitumen	58.4	0.0791	828	1.5624	11.1	0.0263				0.101
6	Bitumen and stone feeding										0.1046
7	Bitumen										0.1921

Bitumen gasification during Run 5 produced an SO_2 emission of 1.56 lb/10^6 Btu (828 ppm). Two factors contributed to this elevated discharge. First, the sulfur content of the bitumen is 50 percent higher than that of the residual oil. Therefore, about 50 percent of the additional SO_2 greater than 300 ppm can be attributed to fuel sulfur content. The second and more important factor was the presence of saturated limestone in the gasifier due to gasifier-regenerator transport duct clogging. This factor was reflected in the regenerator off-gas which contained only 1 percent SO_2. Although fresh limestone was added to the gasifier at about 11:00 a.m. on December 9, stack sampling was performed earlier in the day when the sulfur recovery efficiently (SRE) was abnormally low.

Sulfur trioxide emissions, for which there are no NSPS, increased only about 40 percent in response to stone saturation. The mechanism for SO_3 formation in combustion systems is not yet established. Three pathways have been proposed:

- Gas-phase reaction between SO_2 and O_2;
- Catalytic oxidation on particulate surfaces;[*]
- Gas-liquid reaction on water droplets.

Of the four species necessary for SO_3 formation, water, oxygen and particulate increased only slightly from Run 3 to Run 5. The fact that SO_3 increased by only 40 percent in the presence of an almost 300 percent increase of SO_2 could be taken to indicate that the rate of the reaction to form the trioxide is less than first order in SO_2.

$\underline{NO_x}$

NO_x emissions result from two reactions occuring within the gasifier and the boiler:

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[*] In fact SO_3 is made commercially by passing SO_2 and O_2 over a V_2O_5 catalyst.

$$\text{Fuel bound N} + 1/2\ O_2 \rightleftarrows \text{NO} \equiv \text{Fuel-N conversion}$$

and

$$\text{Atmospheric } N_2 + O_2 \rightleftarrows 2\text{NO} \equiv \text{Thermal fixation}$$

Both reactions require a high temperature environment. Fuel-N conversion proceeds at normal combustion temperatures and is weak function of temperature. Thermal fixation, on the other hand, is highly temperature-dependent,[6] with the rate of NO formation increasing significantly above 980°C (1800°F).

In the relatively low temperature, 900°C (1650°F) environment of the gasifier the thermal fixation reaction is very inefficient. In fact, studies of NO_x formation in fluidized bed combustion of coal[6] in which the oxygen concentrations is in excess of stoichiometric indicate that at this temperature almost all NO_x produced is formed from fuel nitrogen conversion. Measured stack NO_x emissions include not only NO_x formed in the gasifier but also that produced in the high temperature boiler, where thermal fixation is likely the primary source of NO_x.

The average NO_x emission rate during Runs 1, 2 and 5 of 53.5 ppm is considerably lower than the low end of the emission rate range found for conventional oil and gas-fired boilers.[6] This measured rate is also about one-fourth of the NSPS for oil-fired boilers and one-third of the NSPS for gas-fired boilers.[5] Furthermore, the relative invariance of the three measurements suggests a low correlation between the NO_x emission rate and temperature, excess oxygen, bed stone history and fuel.

Several factors may contribute to the low absolute NO_x emission rate. The reducing atmosphere may severely inhibit oxidation of fuel nitrogen. It has also been suggested[6] that limestone might catalytically aid in the decomposition of NO or react directly with NO. The presence of nitrogen on the surface of some of the smaller particulate (which is noted later in the section) is consistent with this latter mechanism. It is also possible that reduced nitrogen species, such as NH_3, formed in the gasifier pass through the boiler without reacting. It is more difficult to explain away the apparently small amount of NO formed by thermal fixation in the boiler. The rate of tube thermal fixation reaction is strongly affected by boiler design and firing characteristics which cannot easily be evaluated.[7]

Two uncertainties are thus apparent. What is the fate of the fuel bound nitrogen which is not converted to NO_x? How will the rate of the thermal fixation reaction be affected by the particular characteristics of the boiler to be used in conjunction with the demonstration plant?

H_2S

No hydrogen sulfide was detected during the first two oil gasification runs and only a quarter of ppm was found in the third run. Thus, H_2S does not present a pollution problem for the CAFB.

Particulate

The primary source of particulate emissions from the CAFB is gasifier bed stone which passes through the two internal cyclones, the knockout baffle and the stack cyclone. The NSPS for particulate emissions from oil-fired boilers is 0.1 $lb/10^6$ Btu. Inspection of Table 29 shows that during oil gasification two of the four runs produced emissions only a few percent below the standard. The NSPS was exceeded during bitumen gasification and combustion; the final bitumen gasification run exceeded the particulate standard by a factor of two. Two factors must be invoked to understand the variation in and magnitude of particulate emissions:

- Cyclone efficiency
- Fresh stone feed.

As noted earlier, cyclone malfunction occured frequently during all runs. In addition, ERCA personnel reported that the cyclones installed at the pilot plant were very old and were not designed specifically for the CAFB system. ERCA estimates stack cyclone efficiency of 50 percent. The high emission rate from Run 7 can be attributed to an unusually high fresh stone feed rate. This stone feed rate will be typical of CAFB start-up procedure. Fresh stone undergoes attrition as it enters the gasifier while being transformed from carbonate to oxide. This start-up condition will normally occur in conjunction with gasifier combustion (see Section II) but was employed during Run 7 to compensate for the buildup of saturated stone due to the clogging of the gasifier-regenerator stone transfer duct. Similar stone addition occurred during pilot plant Run 5, but particulate sampling took place earlier in the day.

Figures 18 and 19 are bar graphs of particulate size distributions for fuel oil and bitumen gasification, respectively. Figure 20 presents these data in log-normal format. These distributions indicate that a substantial fraction of the particulate emissions are in the respirable range and hence of primary concern. The large respirable fraction is typical of conventional cyclones and may be expected in emissions from the demonstration plant which will also employ cyclones for particulate control.

It is difficult to predict particulate loading and size distribution for the demonstration plant and 250 MW unit. Foster-Wheeler claims cyclone design efficiencies of 98 percent, but extensive testing during normal gasification and startup will be necessary to establish actual efficiencies. The abnormally high particulate emission rate observed during fresh stone feed at the pilot plant will have to receive special attention in the demonstration program.

LABORATORY RESULTS

Three types of laboratory analyses were performed on the samples listed in Table 20. The decisions regarding which samples to analyze by which technique were made based upon: importance of information to be gained; availability of previous analyses; cost of analysis; availability of

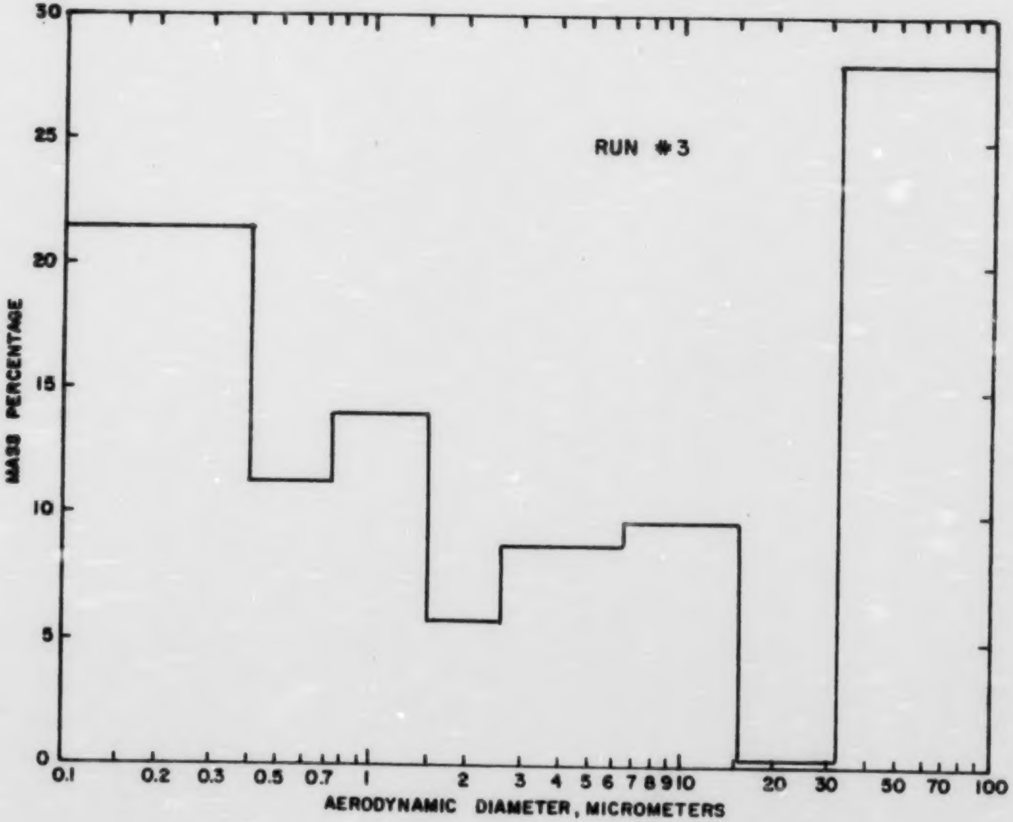

Figure 18. Stack particulate size distribution, Run No. 3.
Fuel oil gasification

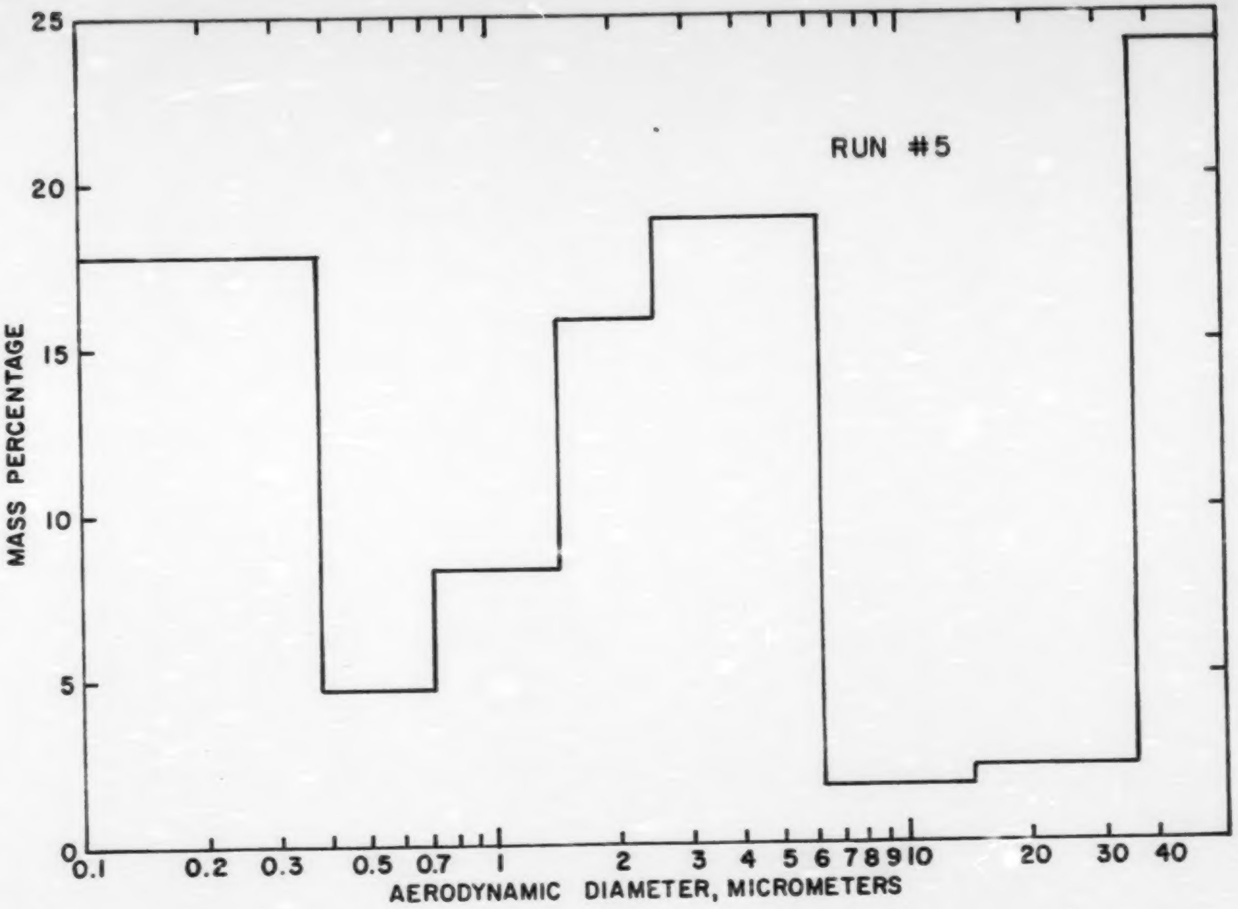

Figure 19. Stack particulate size distribution, Run No. 5. Bitumen gasification

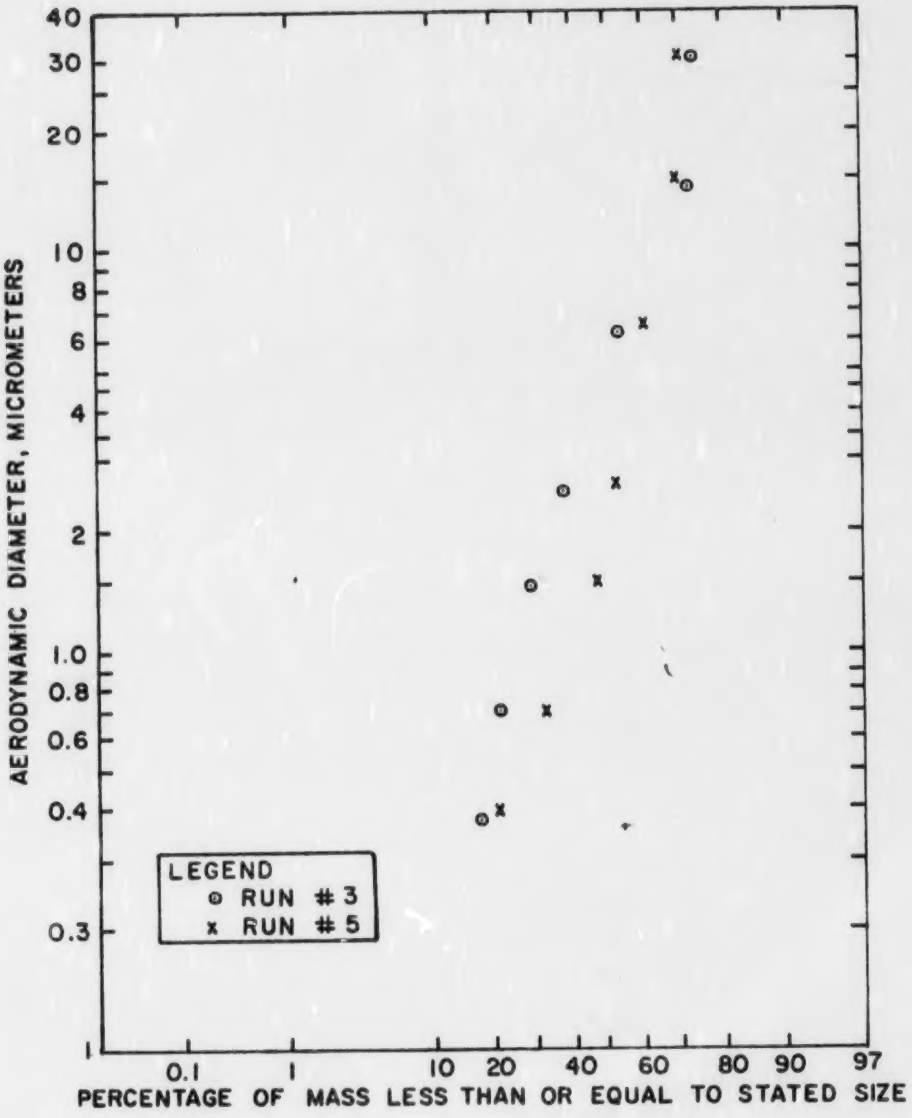

Figure 20. Log-normal particulate size distributions

additional analytical support.[*] Because the emphasis in the present study is on boiler stack emissions, laboratory work was directed toward characterization of the organic and inorganic chemical nature of stack particulate and gases. Nevertheless, to extend the investigations by ERCA and Westinghouse on the nature of spent stone, regenerator bed and gasifier bed samples were analyzed for organic functional group and for surface elements and compounds. Table 30 lists the types of analyses performed on samples collected during the field trip (see also Table 20). Bitumen sample results and fuel oil sample results are presented separately below.

Bitumen Gasification

Bitumen - The organic functional group composition of bitumen was investigated to assess the potential effects of fugitive emissions from storage and handling (see also Section IV). As with all organic analyses reported in this section, the liquid chromatography - infrared spectroscopy (LC/IR) technique described earlier was employed. Figures 21 through 28 are the IR spectra of the eight separable fractions. The distribution of material among the eight fractions is listed in Table 31. Because bitumen is entirely extractable, this distribution is effectively a complete organic analysis of the fuel.

Of the groups tentatively identified in bitumen, POM, phenol and quinone are of particular concern as fugitive species. No MEGS ahve been established for POM, but in general, any amount of these carcinogenic species is considered dangerous. Table 32 summarizes the health effects of several classes of organic compounds and lists their MEGS. Phenol and quinone emissions present potential problems because of their relatively high vapor pressures at the temperature at which bitumen is handled; the low MEG of quinone makes emissions of this compound particularly pernicious. In fact, the high temperature of bitumen storage and handling dictates

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[*] Through PMB/EPA Contract No. DA-6-99-H606A for ESCA analyses.

Table 30. SAMPLE ANALYSES

Sample	Type of analysis			
	Code	Organic	Trace element	Surface
Bitumen	BIT	X		
Fuel oil	FO5	X	X	
Limestone	LSS			X
Regenerator bed stone				
Run no. 4	RB8	X	X	X
Run no. 5	RB9	X	X	X
Gasifier bed stone				
Run no. 2	GB5		X	X
Run no. 5	GB9	X	X	X
Left-hand cyclone particulate				
Run no. 2	LH5			X
Run no. 4	LH8	X		
Right-hand cyclone particulate				
Run no. 5	RH9		X	X
Knockout baffle particulate				
Run no. 3	KO6		X	
Run no. 5	KO9	X	X	X
Stack cyclone particulate				
Run no. 4	SC8	X	X	X
Run no. 5	SC9	X	X	X
Gaseous effluent				
Run no. 4	GE8			
Run no. 6	GE0			
Run no. 7	GE1	X		
Leached stone[a]				
	SS1			X
	SS3			X
	SS5			X

Table 30 (continued). SAMPLE ANALYSIS

Sample	Type of analysis			
	Code	Organic	Trace element	Surface
Method 5 train, filter catch				
Run no. 1				X
Run no. 2				X
Run no. 3				X
Run no. 4				X
Run no. 5				X
Run no. 6				X
Run no. 7				X
Impactor substrates				
Run no. 3				
Stage 1	UW61			X
Stage 2	UW62			X
Stage 3	UW63			X
Stage 4	UW64			X
Stage 5	UW65			X
Stage 6	UW66			X
Stage 7	UW67			X
Backup filter	UW68			X
Impactor substrates				
Run no. 5				
Stage 1	UW91			X
Stage 2	UW92			X
Stage 3	UW93			X
Stage 4	UW94			X
Stage 5	UW95			X
Stage 6	UW96			X
Stage 7	UW97			X
Backup filter	UW98			X

[a] See Table 21.

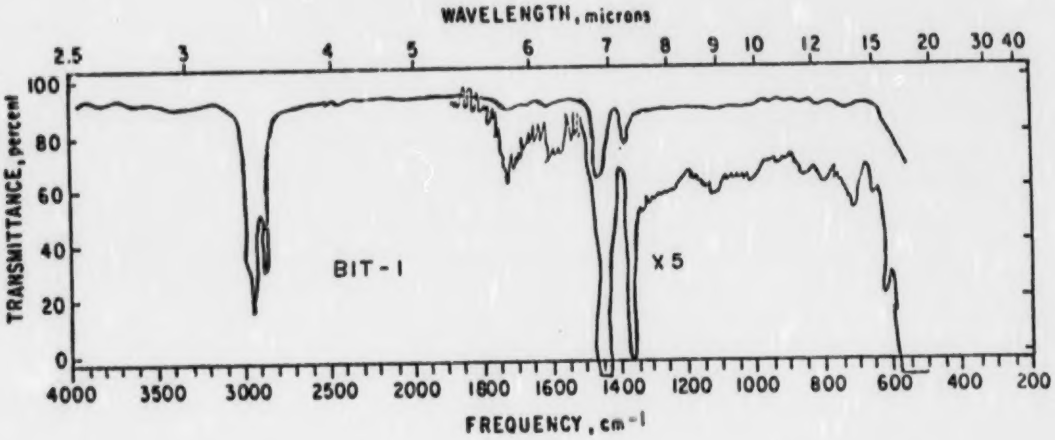

Figure 21. Bitumen, LC fraction 1. Peak at 2920 cm^{-1} and peaks at ~1450 cm^{-1} and 1370 cm^{-1} are from CH_3, CH_2. Bands at ~1600 cm^{-1} and 1690 are typical of asphaltic materials. 1690 cm^{-1} band is from gross mixture of carbonyls whereas 1600 cm^{-1} band is due to structures such as highly condensed aromatics and quinones

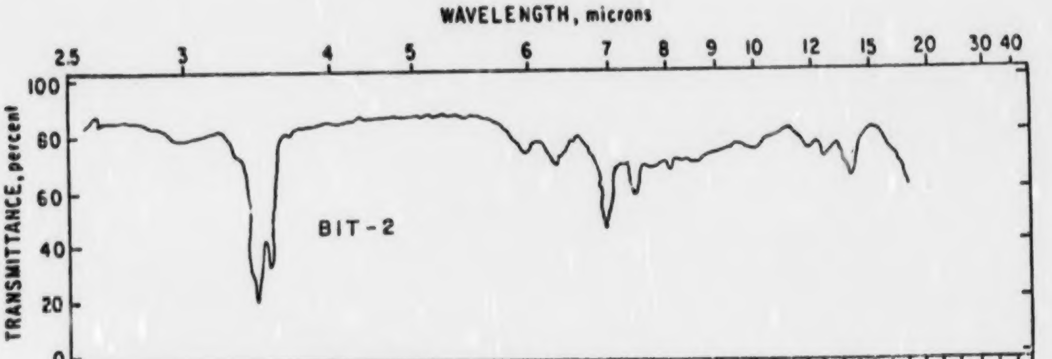

Figure 22. Bitumen, LC fraction 2. See Figure 21. Bands between 700-900 cm^{-1} indicate aromatic compounds (possibly POM)

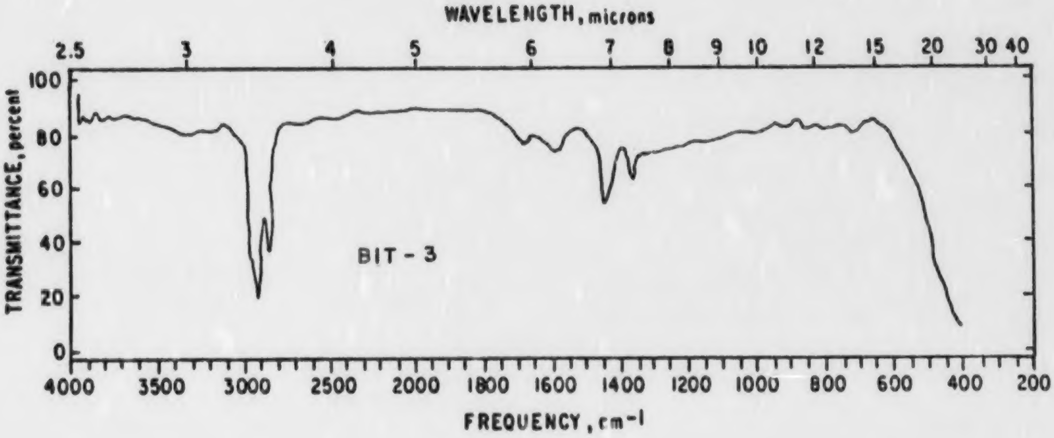

Figure 23. Bitumen, LC fraction 3. See Figure 21

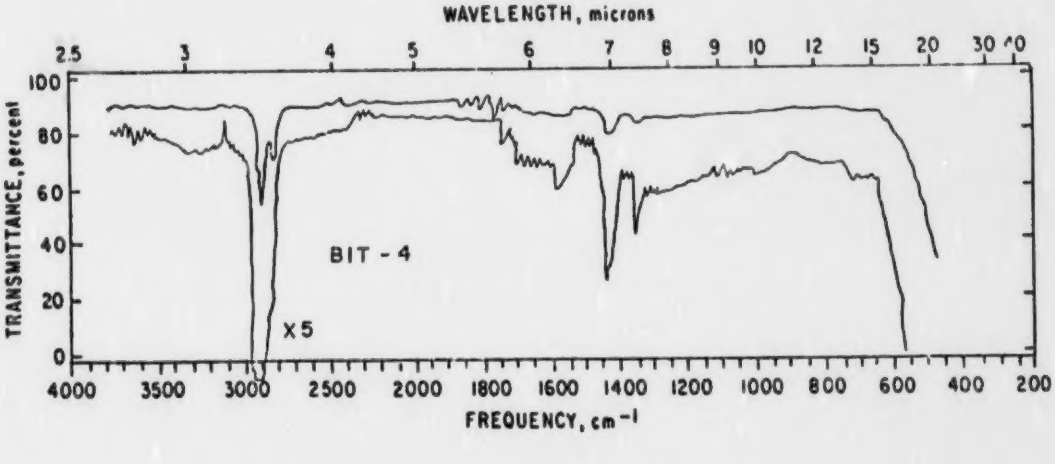

Figure 24. Bitumen, LC fraction 4. See Figure 21. This spectra indicates asphaltic and carbonyl compounds

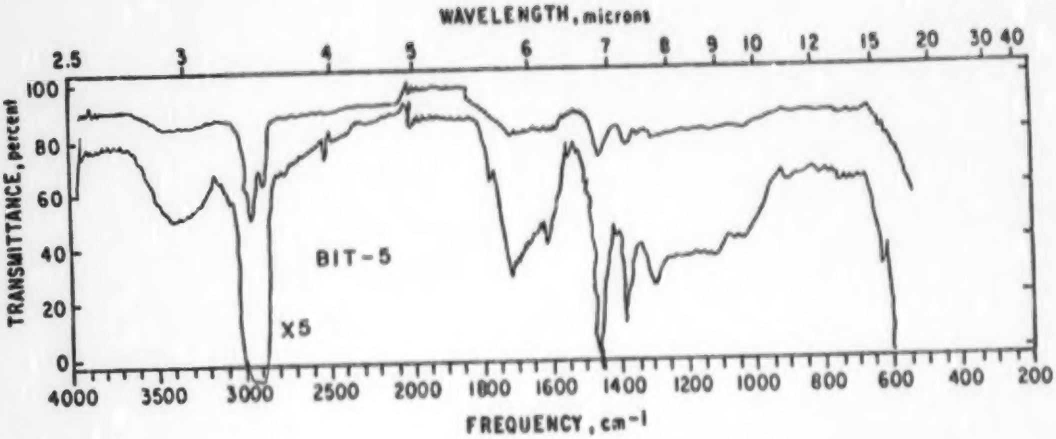

Figure 25. Bitumen, LC fraction 5. Strong band at ~3400 cm^{-1} indicates -OH. Band between 1200-1300 cm^{-1} suggests this might be present as phenol

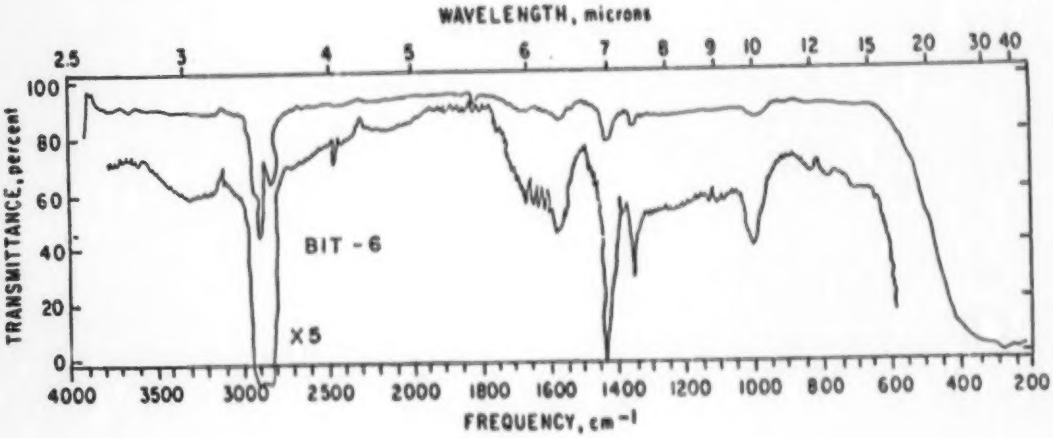

Figure 26. Bitumen, LC fraction 6. See Figure 21. Band at 1025 cm^{-1} probably from SiO_2 impurity

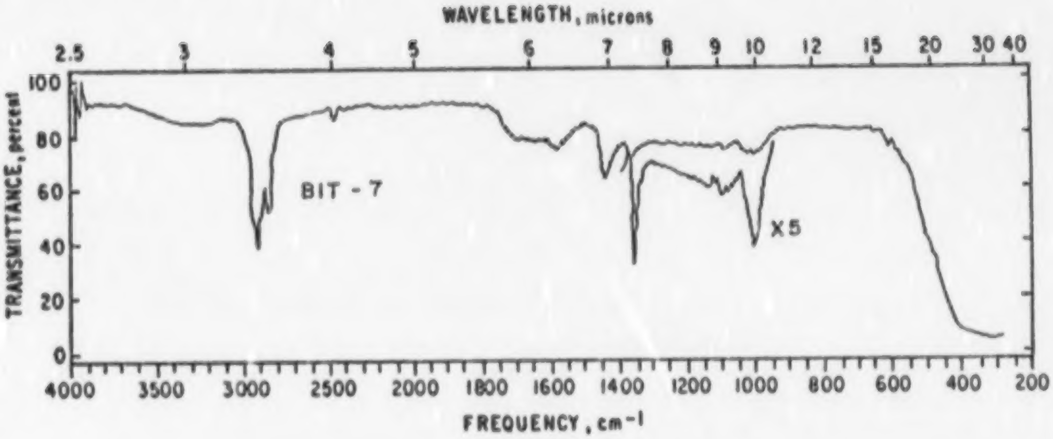

Figure 27. Bitumen, LC fraction 7. See Figure 21. 1025 cm^{-1} probably from SiO_2 impurity

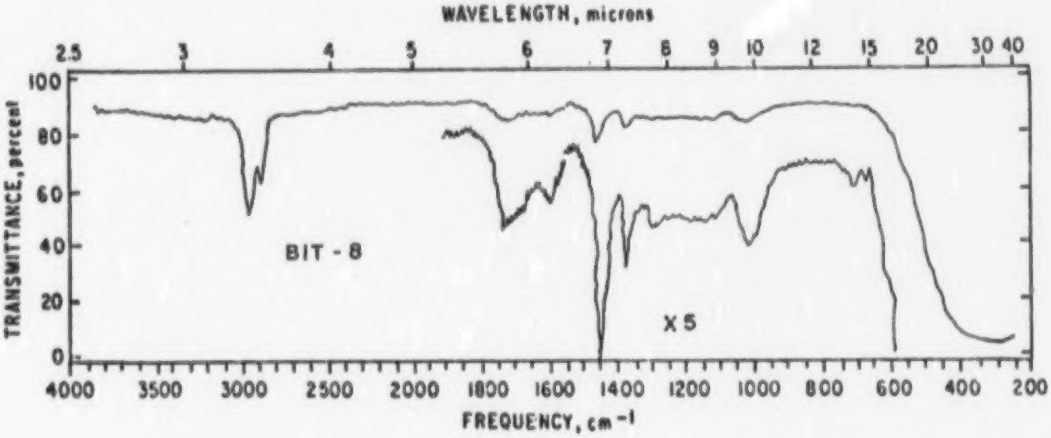

Figure 28. Bitumen, LC fraction 8. See Figure 21. Band at 1025 cm^{-1} probably from SiO_2 impurity

Table 31. DISTRIBUTION OF MATERIAL AND FUNCTION GROUPS IN BITUMEN

Fraction	Weight, μg	Percent	Functional groups
1	8,900	67.0	1. Aliphatic hydrocarbons, asphaltenes, carbonyls, highly condensed aromatics, quinones.
2	890	6.7	2. Aromatics (possibly POM)
3	810	6.1	3.
4	350	2.6	4. Asphaltenes, carbonyls
5	280	2.1	5. Phenol
6	1,400	10.5	6.
7	210	1.6	7.
8	450	3.4	8.
Total	13,290	100	

Table 32. HEALTH AND ECOLOGICAL EFFECTS AND MEGS OF ORGANIC COMPOUND CLASSES

Generic class	Effects	Phase	MEG	Ref.
Hydrocarbons Ex: Ethylene	Threshold effects on plants - reduced growth, premature senescence and reduced flowering and fruit production.	Gas	11 $\mu g/m^3$ [a]	17
Alcohols Ex: Ethyl alcohol	Irritant to eyes and mucous membrane. Repeated contact produces dry, scaly, and fissured dermatitis. Causes intoxication when inhaled at high concentrations.	Gas	6.3 mg/m^3	18
Phenols Ex: Phenol	Primary irritant having strong corrosive properties for all body tissue. Acute poisoning mainly characterized by central nervous tissue manifestations. Pneumonia, renal and hepatic damage frequently follow phenol intoxication.	Gas	63 $\mu g/m^3$	18
Phthalate Ex: Phthalic anhydride	In a pure state, it is not an irritant, but in contact with water, the caustic phthalic acid is formed. Irritation may produce conjunctivitis contact dermatitis, atrophy of the nasal mucous membrane, loss of sense of smell and hoarseness. Bronchitis, emphysema and asthma may occur.	Particulate and gas	40 $\mu g/m^3$	18
Esters and carboxylic acids Ex: Acetic acid	High concentration of vapor produce conjunctivitis, dental errosion and nasal irritation. On contact, glacial acetic acid produces painful burns, repeated contact produces fissured dermatitis. Inhalation may lead to bronchitis and pulmonary edema	Gas	83 $\mu g/m^3$	18
N-Heteroaromatic Ex: Pyridine	Irritating to eyes, nose and throat. acute exposure produces flushing of the face and narcotic effects of nausea, vomiting and dizziness. Effects of chronic exposure include headaches, nervousness, and insomnia.	Gas	50 $\mu g/m^3$	18
Quinone	Condensation of vapor on eyes produces conjunctivitis lacrimation, photophobia, corneal strains, ulcerations and opacities. In animals ingestion of quinone produces convulsions, respiratory difficulties, hypotension and asphyxia	Gas	1.3 $\mu g/m^3$	18
C=O Containing species Ex: Formaldehyde	Irritating to conjunctivia and mucous membranes of upper respiratory tract. Ingestion may result in gastrointentinal irritation. Respiratory depression and death.	Gas	20 $\mu g/m^3$	18
Carboxylic acid salt Ex: Acetic acid, nickel (II) salt	Metallic nickel and its soluble salts are toxic to animals due more to gastrointestinal irritation than to any specific toxicity chronic inhalation of nickel dust produce tumors. Ingestion of nickel by animals reduces reproduction and growth rates.	Particulate		19

that fugitive emission sampling for gaseous organic compounds should be undertaken at the demonstration plant. This point is particularly important because of the variability of fuels which will be available to the CAFB.

Flue Gas - Spectra of gaseous organic stack emissions collected during Run 7 are shown in Figures 29 through 34. Spectra not shown contain no peaks other than those corresponding to aliphatic hydrocarbons (present in all fractions) or to the ubiquitous silicon oil impurity. Table 33 contains the distribution of material between the eight fractions and lists species identified in each. The bulk of the gaseous emissions is a mixture possibly containing disubstituted amide, N-heteroaromatics, doubly conjugated ketones and quinone. Additional, Level 2 organic analysis will be necessary to identify this material.

Gaseous effluent was collected for 53 minutes during which time 0.56 m^3 (19.7 ft^3) of flue gas was pulled through the absorbent column. The concentration of organic species ($<C_5$) in the glue gas was therefore 31.8 mg/m^3 corresponding to an emission rate of 0.7 μg/kcal or 0.022 $lb/10^6$ Btu. Using the dilution factor of 1:1000 noted in Section IV between concentrations at the stack and on the ground, the ground level ambient loading of gaseous organic species becomes 30 $\mu g/m^3$. Comparison of this ambient loading with the MEGS listed in Table 32 indicates that hydrocarbons, quinone and carbonyl compounds are potentially of concern. Final evaluation must await the results of more sophisticated organic analyses.

Stack Particulate - Stack cyclone material was analyzed for organic and inorganic species because insufficient quantities of particulate were collected on the Method 5 filters. Figures 35 through 40 are spectra of the organic material extracted from stack cyclone particulate collected during Run 5. Table 34 summarizes the results of this analysis. Organic material was extracted from a 1 gram particulate sample. Assuming 80 percent extraction/chromatography efficiency, and that the stack

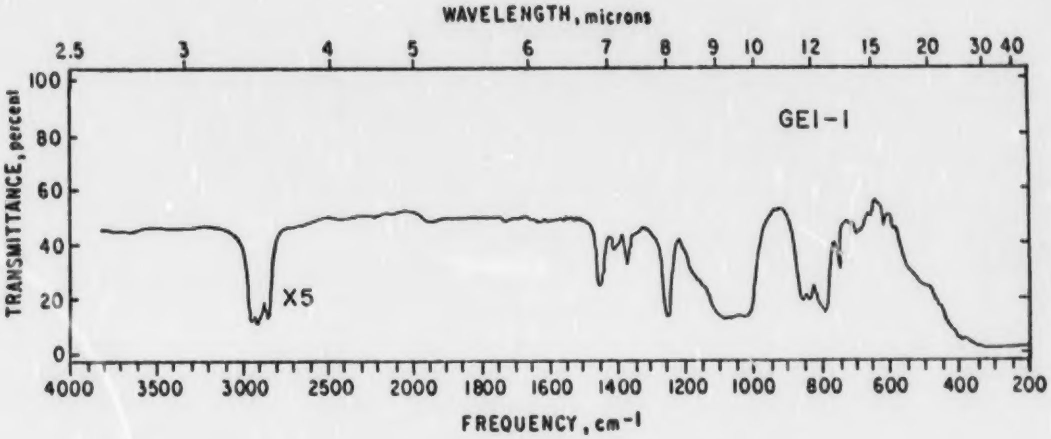

Figure 29. Flue gas from bitumen gasification, Run No. 7, LC fraction 1. Peaks at 2920, 1450 and 1370 indicate aliphatic hydrocarbons. Structure at lower frequencies is due to silicon oil impurity

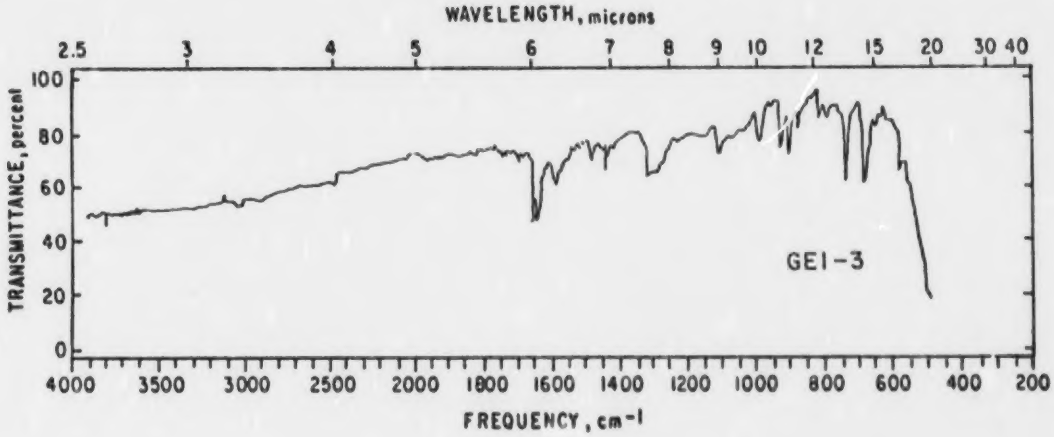

Figure 30. Flue gas from bitumen gasification, Run No. 7, LC fraction 3. Complex spectrum suggests: (1) disubstituted amide, (2) N-heteroaromatic, (3) doubly conjugated ketone, or (4) quinone

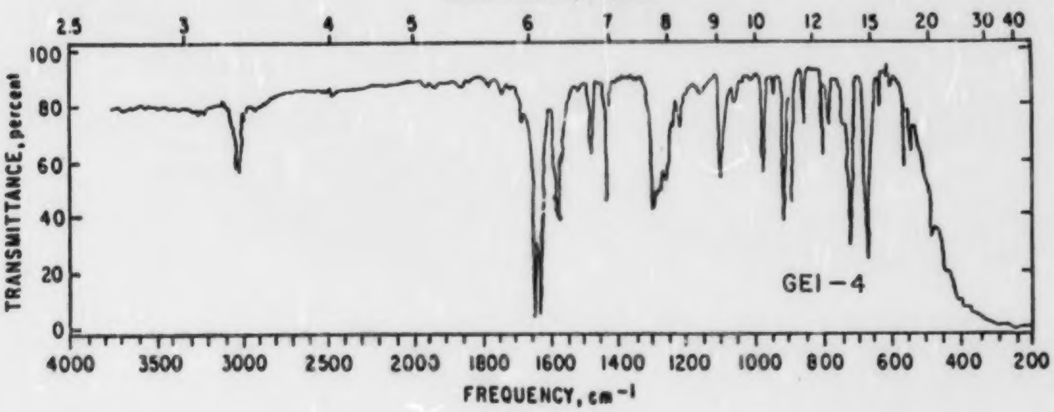

Figure 31. Flue gas from bitumen gasification, Run No. 7, LC fraction 4. See Figure 30

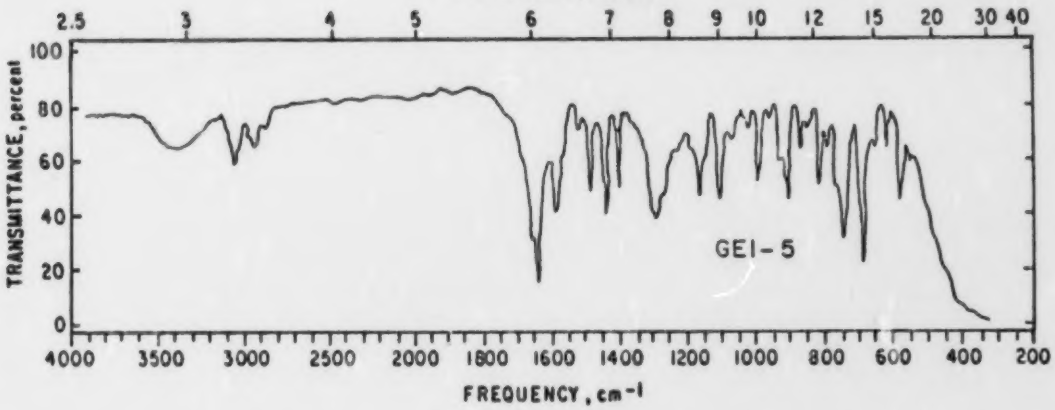

Figure 32. Flue gas from bitumen gasification, Run No. 7, LC fraction 5. See Figure 30. Band at 3400 cm^{-1} suggests presence of alcohol or carboxylate

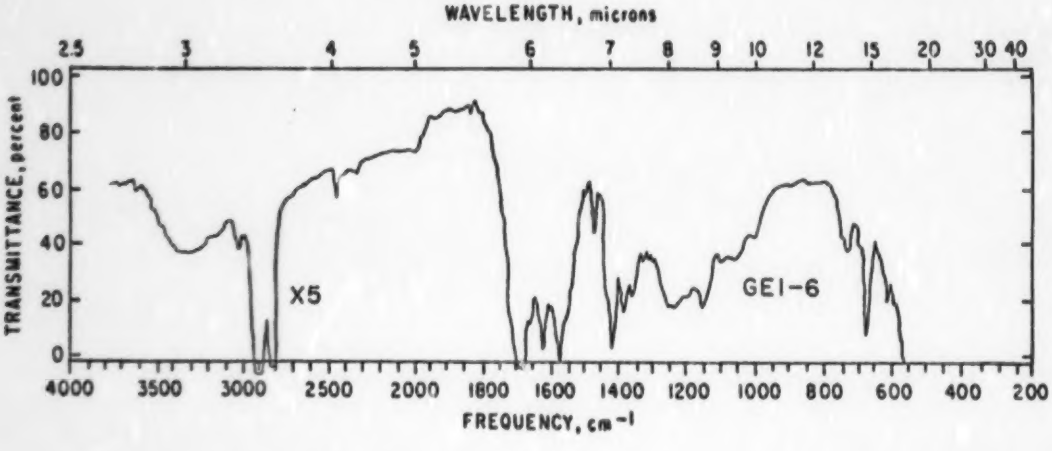

Figure 33. Flue gas from bitumen gasification, Run No. 7, LC fraction 6. Peak at 3400 cm^{-1} indicates carboxylate group. Peak at 1640 cm^{-1} indicates doubly conjugated ketone. Peaks between 600-800 cm^{-1} indicate aromatics

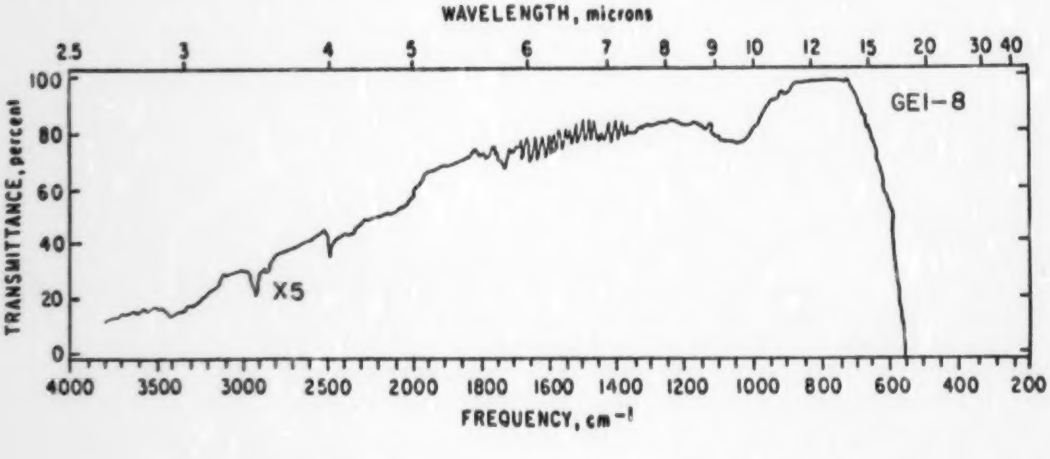

Figure 34. Flue gas from bitumen gasification, Run No. 7, LC fraction 8. Possible traces of carboxylic acid salts. Band between 1000-1100 cm^{-1} probably from SiO_2 impurity

Table 33. DISTRIBUTION OF MATERIAL AND FUNCTIONAL GROUPS IN STACK GAS EFFLUENT: RUN NO. 7

Fraction	Weight, μg	Percent	Functional groups
1	1,700	9.5	Aliphatic hydrocarbons
2	60	0.3	
3	1,600	9.0	Complex mixture
4	13,000	73.0	Complex mixture
5	1,100	6.2	Alcohol or carboxylate
6	250	1.4	Carboxylate, doubly conjugated ketones, aromatics
7	74	0.4	
8	32	0.2	Carboxylic acid salts
Total	17,816	100	

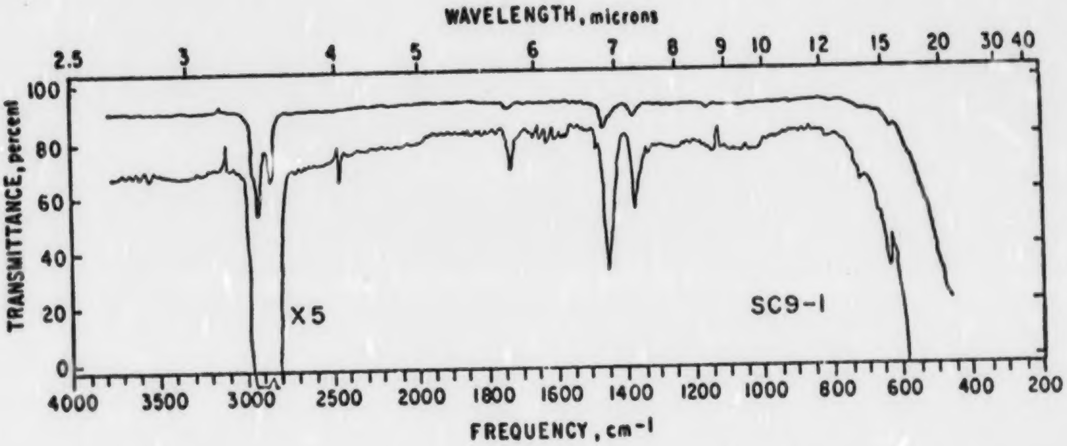

Figure 35. Stack cyclone material from bitumen gasification, Run No. 5, LC fraction 1. Peak at ~2920 cm^{-1} and peaks at 1450 cm^{-1} and 1370 cm^{-1} are from CH_3, CH_2. This indicates presence of aliphatic hydrocarbons. Peak at 1730 cm^{-1} is from C=O

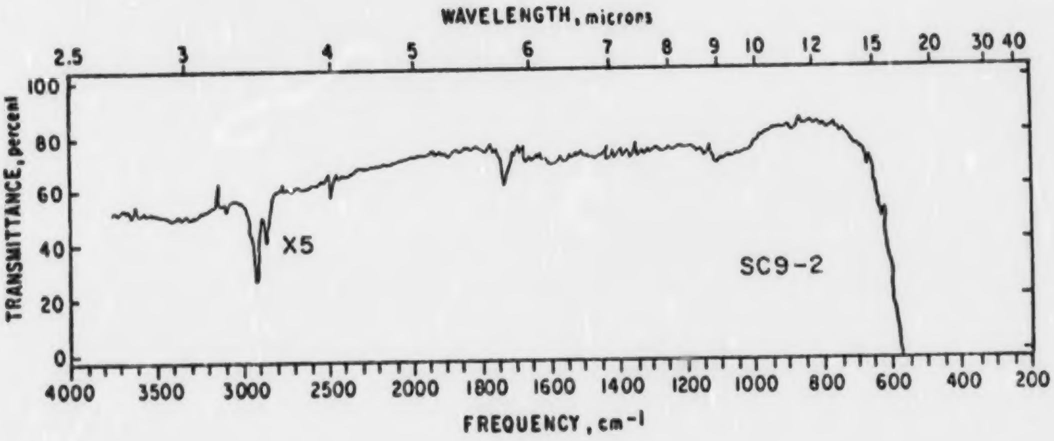

Figure 36. Stack cyclone material from bitumen gasification, Run No. 5, LC fraction 2. Peaks at ~2920 cm^{-1} and 1730 cm^{-1} indicate presence of aliphatic esters

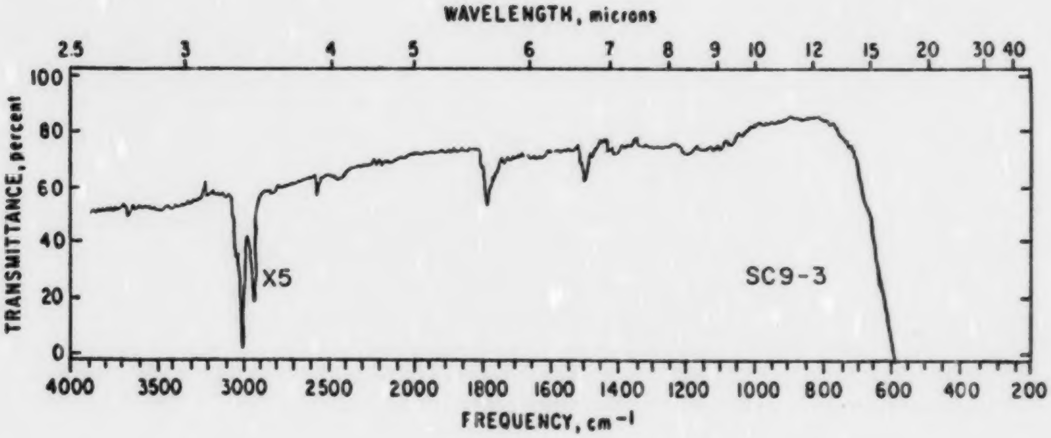

Figure 37. Stack cyclone material from bitumen gasification, Run No. 5, LC fraction 3. Peaks at 1730 cm^{-1} and ~1500 cm^{-1} indicate presence of aliphatic carbonyl compounds

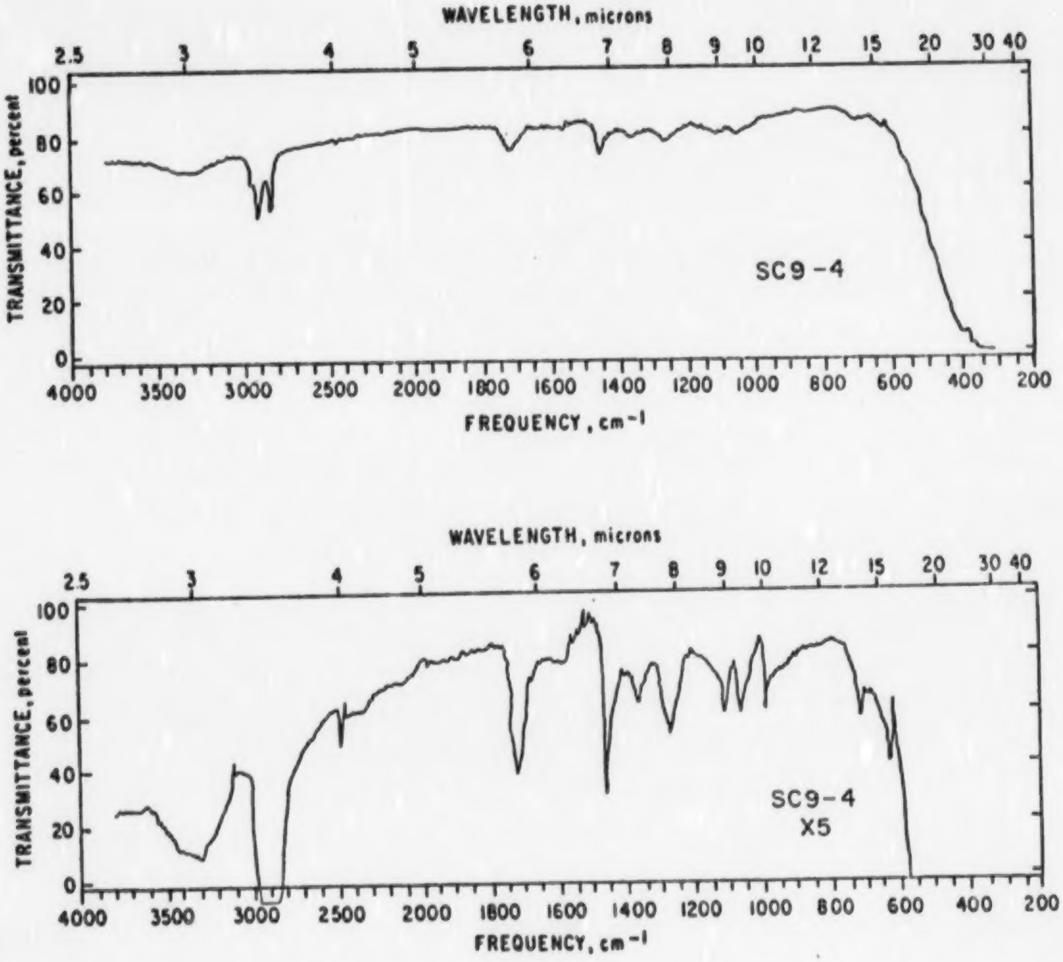

Figure 38. Stack cyclone material from bitumen gasification, Run No. 5, LC fraction 4. Peak at 3400 cm^{-1} indicates -OH; peaks between 600-800 cm^{-1} indicate aromatics; peak at 1730 cm^{-1} indicates carbonyls. Peak at 1500 cm^{-1} and complexity of spectrum between 1000-1300 cm^{-1} indicates possible presence of phthalates, phenols, or alcohols

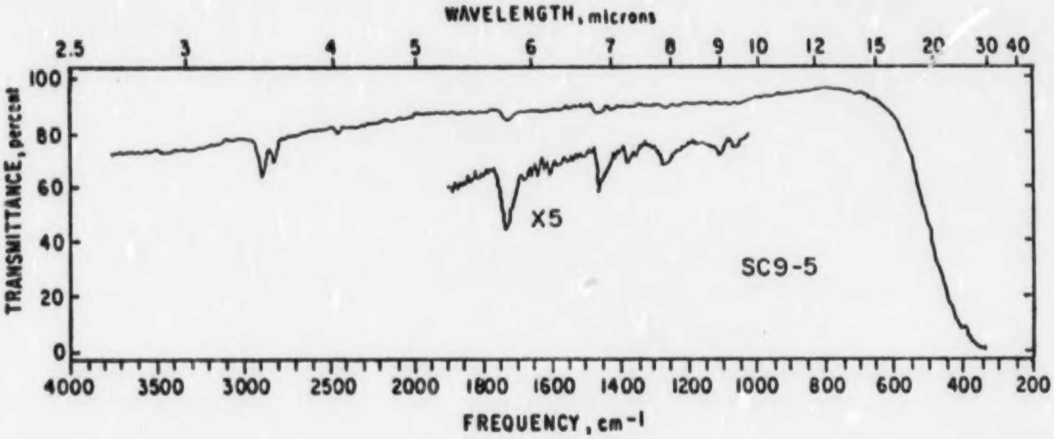

Figure 39. Stack cyclone material from bitumen gasification, Run No. 5, LC fraction 5. See Figure 38.

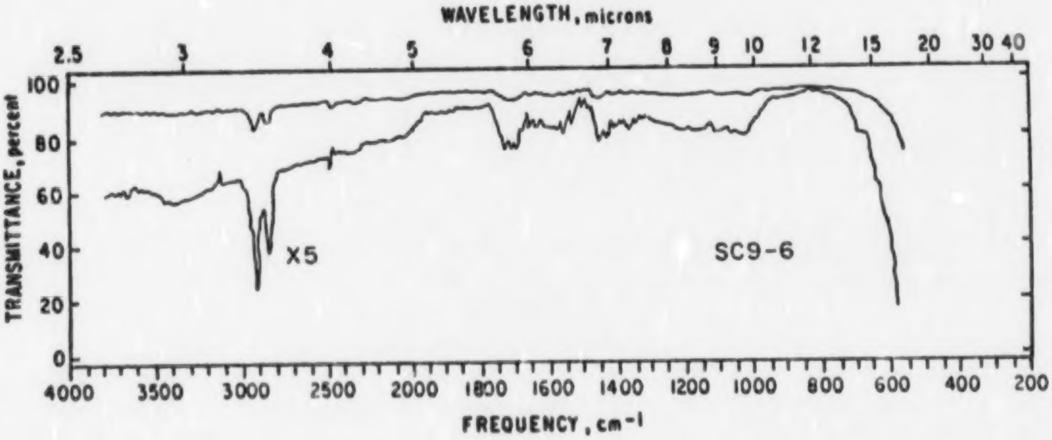

Figure 40. Stack cyclone material from bitumen gasification, Run No. 5, LC fraction 6. Mixture of carbonyl and alcohol compounds

Table 34. DISTRIBUTION OF EXTRACTABLE ORGANIC MATERIAL AND FUNCTIONAL GROUPS IN STACK CYCLONE PARTICULATE: RUN NO. 5

Fraction	Weight, µg	Percentage	Functional groups
1	70	10.7	Aliphatic hydrocarbons, carbonyl
2	14	2.1	Aliphatic esters
3	28	4.3	Aliphatic carbonyls
4	140	21.4	Aromatics, carbonyls, phthalates, phenols, alcohols
5	230	35.2	As in fraction 4
6	66	10.1	Carbonyls, alcohols
7	16	2.4	——
8	90	13.8	——
Total	654	100	

cyclone material is representative of particulate emissions (this is probably a poor assumption because substantial condensation of organic gases on particulate occurs after the stack cyclone where the flue gas has cooled down significantly), 654 μg of organic recovery corresponds to an organic particulate loading of 0.12 mg/m^3 or 7 x 10^{-5} lb/10^6 Btu. This organic emission rate, when compared with the health effects data in Table 32 does not appear to be a potential problem.

The stack cyclone particulate sample was also analyzed for bulk elemental composition by the methods discussed earlier. The results of this analysis is presented in Table 35. The total particulate loading during Run 5 was 0.141 gm/m^3. Multiplying the concentrations listed in Table 35 by this number yields the concentration of trace elements in the flue gas. For all metals, the result is less than the worst case analyses emission factor listed in Table 9.*

The only element whose particulate abundance is larger than the worst case prediction is fluorine 0.06 mg/m^3 versus 0.014 mg/m^3. Fluorine was also found in the analysis by ERCA of stack cyclone particulate from a previous pilot plant run (private communication); however in that case the fluorine concentration was between 6 and 60 ppm (compared to 450 ppm here). In the present case three possible explanations for "violation" of the worst case result can be given. Worst case analyses displayed in Section IV were based upon analyses for fuel oil and limestone reported in Tables 4 and 6. No trace element analysis is available for bitumen; fluorine may be much more abundant in this fuel than in No. 6 oil. It is also possible that ERCA's analysis of limestone is in error. Their analysis indicates an upper limit of 2 ppm for fluorine but also indicates the presence of an interference. If fluorine were present at a

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*Although the values in Table 9 were calculated based upon No. 6 oil as the fuel, trace metal concentrations in bitumen will not differ significantly.

Table 35. MASS SPECTROGRAPHIC AND ATOMIC ABSORPTION SPECTROMETRIC ANALYSIS OF STACK CYCLONE PARTICULATE RUN NO. 5

Element[a]	Concentration, ppmw or percent
Ca[c]	14.1 %
S[b]	3.83
V[c]	1.04
Si	0.49
Na	0.43
Mg	0.32
Ni[c]	0.22
Fe[c]	0.12
F	450 ppmw
K	340
Al	340
Cl	120
Ti	63
Ba	55
Cr	51
Cu	33
Sr	32
Zn	30
P	21
Mn	21
Co	17
Pb	7.8
Mo	5.0
Li	4.3
Ge	4.1
B	2.3
Br	2.2
Zr	1.5
Se	1.3

Table 35 (continued). MASS SPECTROGRAPHIC AND ATOMIC ABSORPTION SPECTROMETRIC ANALYSIS OF STACK CYCLONE PARTICULATE RUN NO. 5

Element[a]	Concentration, ppmw or percent
I	1.3 ppmw
Rb	1.1
Ce	0.6
Yb	<0.5
Ga	0.4
Bi	0.4
Ta	0.4
Cd	0.3
Sn	0.3
W	<0.3
Hf	<0.3
Tl	0.2
Y	0.2
La	0.2
Th	<0.2
Dy	<0.2
Sm	<0.2
Be	<0.12
Nb	0.1
Nd	0.1
Pr	<0.1

[a] Elements not listed are <0.1 ppm, not detected.

[b] Determined by wet chemistry.

[c] Determined by atomic absorption spectrometry.

[d] Used as internal standard.

level of 2 ppm the worst case analysis would still yield an upper limit of also 0.025 mg/m^3. Another explanation for the apparently high fluorine content of particulate is that the fluorine concentration measured by SSMS is artificially high due to interfering contributions to apparent mass 19 by organic ions. Nevertheless, if the fluorine concentration reported in Table 35 is correct, the resultant ambient loading is still too low to be of concern (see Table 9).

In Section IV it was pointed out that vanadium, cadmium and nickel are the only metals whose worst case emission factors are of concern. The actual vanadium emission factor is 0.141 gm/m^3 x 0.0104 = 1.5 mg/m^3 which is 1.5 μg/m^3 at ground level or 88 percent of its MEG. This is equivalent to 3.4 percent of the vanadium content of bitumen. This finding is very critical because the vanadium emission factor might increase during prolonged operation with the stone transfer system clogged. Thus, the claim that bed material accumulates almost 100 percent of the fuel vanadium is somewhat misleading because particulate emissions which are representative of bed stone contain this significant quantity of vanadium. Cadmium and nickel emission factors are much less than their MEGS and, hence, need no additional control.

To pursue the nature of the particulate emissions further, ESCA spectra were taken of these stack cyclone particulates as well as of material caught by the hi-vol filter and that deposited on each stage of the impactor. Figures 41 and 42 are broadband scans of stack cyclone (SC9) and filter (FS9) particulate. It is apparent that both samples are heavily coated with carbonaceous material. This coating is the result of incomplete combustion coupled with deposition of organic material at all stages of the process, particularly in the cooler stack region. Table 36 summarizes the surface elemental abundances of these samples as well as results of scans of each impactor substrate stage (particulate size decreases from UW91 to UW98). In addition to analyzing surface properties, several impactor substrate samples were sputtered down to ~ 100 Å and rescanned. The results of these spectra are labelled "subsurface" in

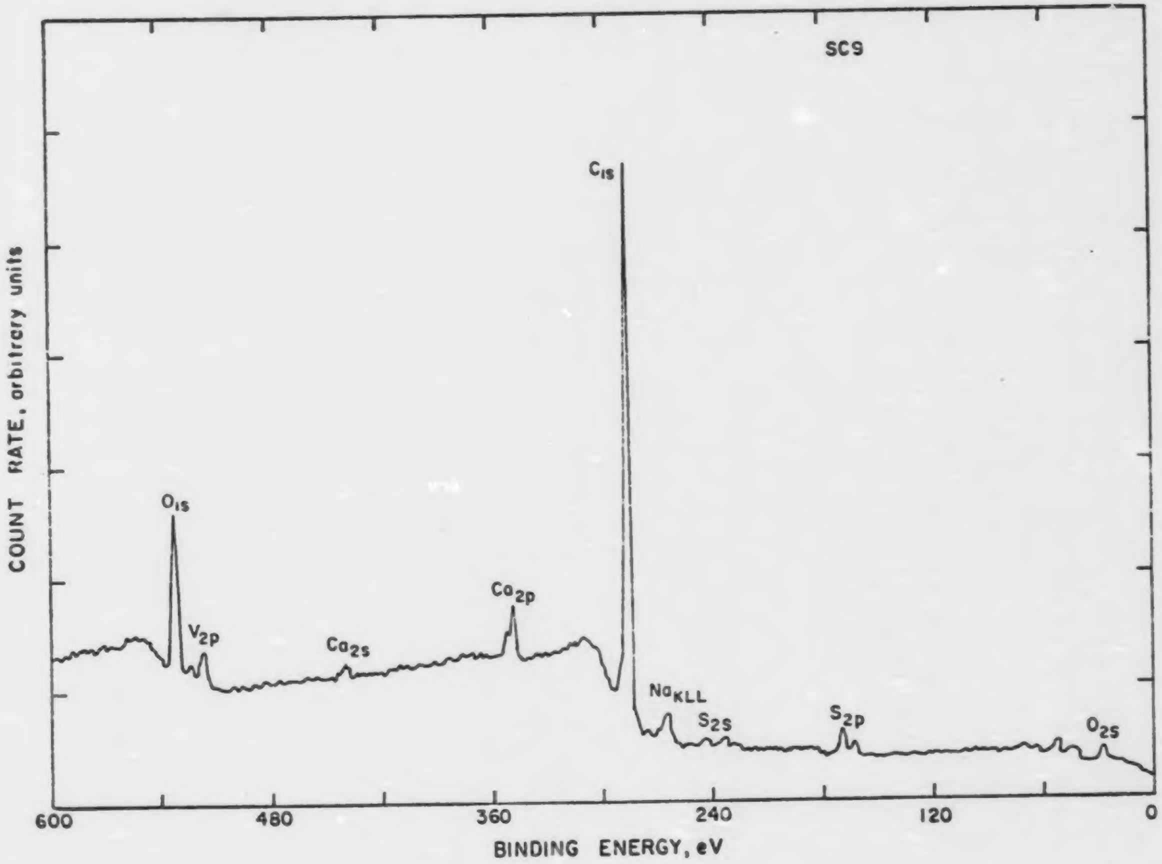

Figure 41. Stack cyclone material from bitumen gasification, Run No. 5. Broadband ESCA scan

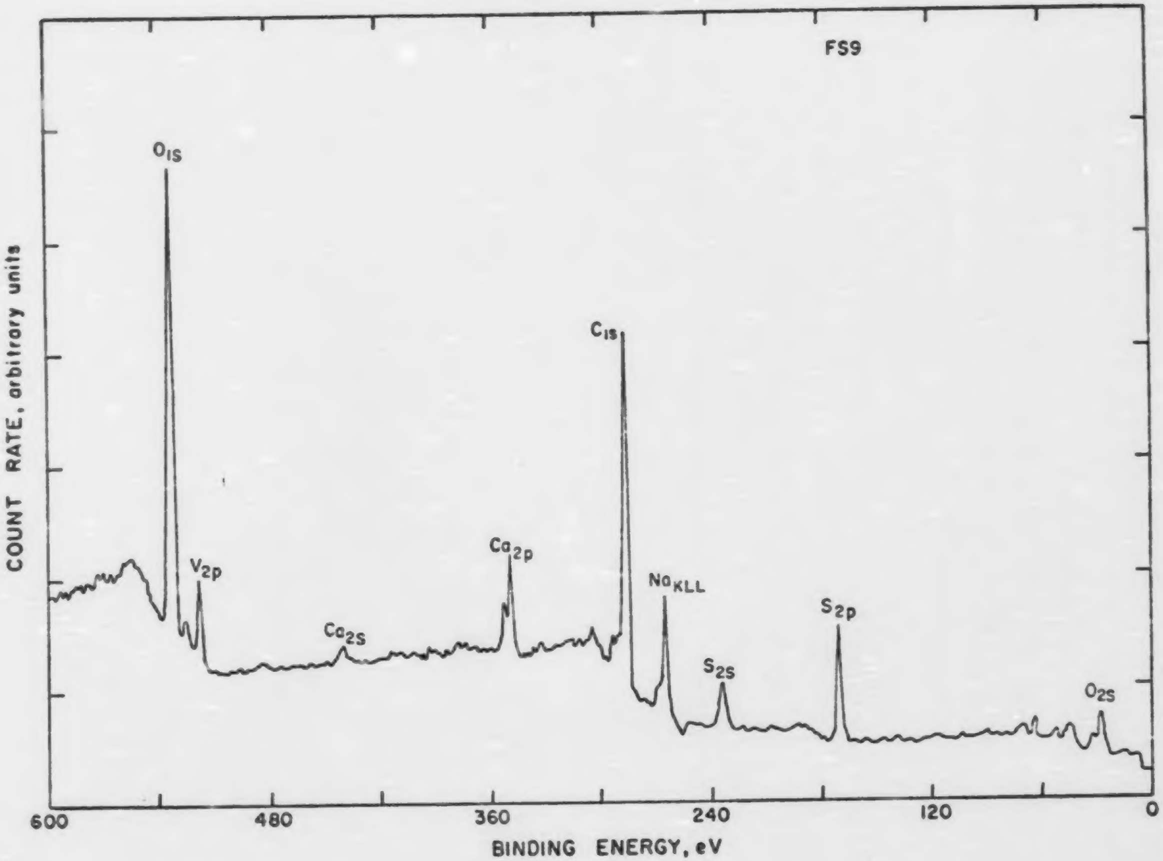

Figure 42. Stack sampling train filter material from bitumen gasification, Run No. 5. Broadband ESCA scan

Table 36. The subsurface scans indicate that the bulk of the carbon on the small particulate is on or near the surface, reinforcing the hypothesis that a significant portion of the organic material condenses in the stack. (The results for the smallest particulate, UW98, are anomalous in this regard. This may indicate that these particles are in fact mostly carbonaceous material, rather than attributed stone.) It is also interesting to note the relatively high surface sulfur concentrations. Again this could be due to condensation of sulfur oxides in the stack.

Vanadium surface and subsurface concentrations are on the order of bulk values (see Table 35), with subsurface values appearing higher due to removal of surface carbon. Sodium is considerably more abundant on the surface than in bulk. Surface enrichment of sodium is well known[10] and is due to vaporization of sodium compounds in the gasifier and subsequent condensation of these species in the cooler stack. A similar surface enrichment phenomenon has been found for vanadium[10] but is not evident from the particulate results. However, it will be noted later that surface vanadium in gasifier bed material and larger particulate (that captured by the gasifier cyclones) is less than 0.2 percent, thus indicating that smaller particulate surfaces are preferentially enriched in vanadium.

Also included in Table 36 are the results of broadband scans of filter particulate collected during Run 7 (FS1). The surface abundances on sample FS1 are almost identical to those from FS9. The similarity between subsurface and surface abundances on FS1 differs from the results of the impactor substrate studies but is consistent with the results of filter particulate collected during fuel oil gasification (which is discussed later in this section).

To determine the compound form of vanadium the cyclone and filter samples were scanned over the binding energy range corresponding to ejection of the 2p electron of vanadium. These spectra are shown in Figures 43 and 44. Comparison of these spectra with standards V_2O_5 and vanadium metal (Figures 15 and 16) indicates that a mixture of oxides presumably

Table 36. SURFACE AND SUBSURFACE CONCENTRATIONS OF STACK PARTICULATE COLLECTED DURING BITUMEN GASIFICATION

Element	Sample, % abundance																
	SC9[a]	FS9[a]	UW91[a]		UW92[a]	UW93[a]		UW94[a]	UW95[a]		UW96[a]	UW97[a]		UW98[a]		FS1[b]	
	Surface	Surface	Surface	Sub-surface	Surface	Surface	Sub-surface	Surface	Surface	Sub-surface	Surface	Surface	Sub-surface	Surface	Sub-surface	Surface	Sub-surface
O	12.8	34.6	34.2	61.0	28.8	37.4	67.9	32.1	34.4	65.9	32.1	35.4	63.8	14.1	10.5	36.0	33.1
V	1.1	2.4	0.7	1.0	0.4	0.5	0.9	0.6	0.4	0.9	0.4	0.5	1.3	0.3	1.9	2.1	1.3
N	-	-	3.3	-	2.7	2.3	-	3.1	2.2	-	3.2	2.7	-	-	-	-	-
C	80.8	49.8	52.4	31.5	60.7	50.1	26.1	56.2	55.1	28.1	55.6	52.9	30.5	82.4	83.9	48.5	51.5
Na	0.8	2.9	1.4	0.9	1.0	1.3	0.9	1.5	1.1	0.8	1.6	1.6	1.3	0.8	0.8	2.5	1.8
S	3.1	7.7	7.9	4.2	6.4	8.3	2.9	6.5	7.0	2.8	7.1	6.9	2.4	2.5	2.8	6.2	5.1
Ca	1.5	2.6	-	1.4	-	-	1.2	-	-	0.7	-	-	0.7	-	-	4.8	6.9

[a] Run 5.

[b] Run 7.

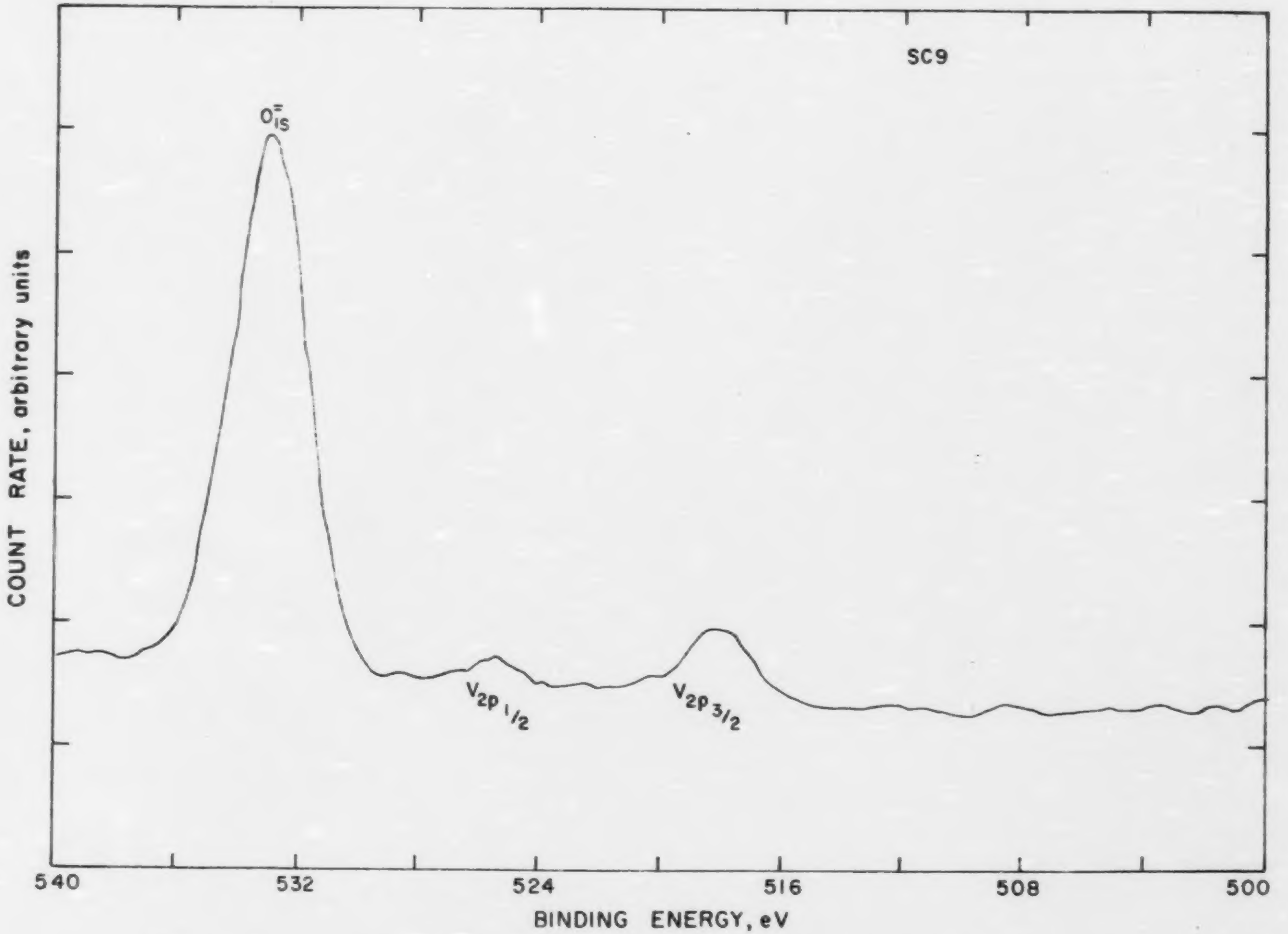

Figure 43. Stack cyclone material from bitumen gasification, Run No. 5. Vanadium ESCA scan

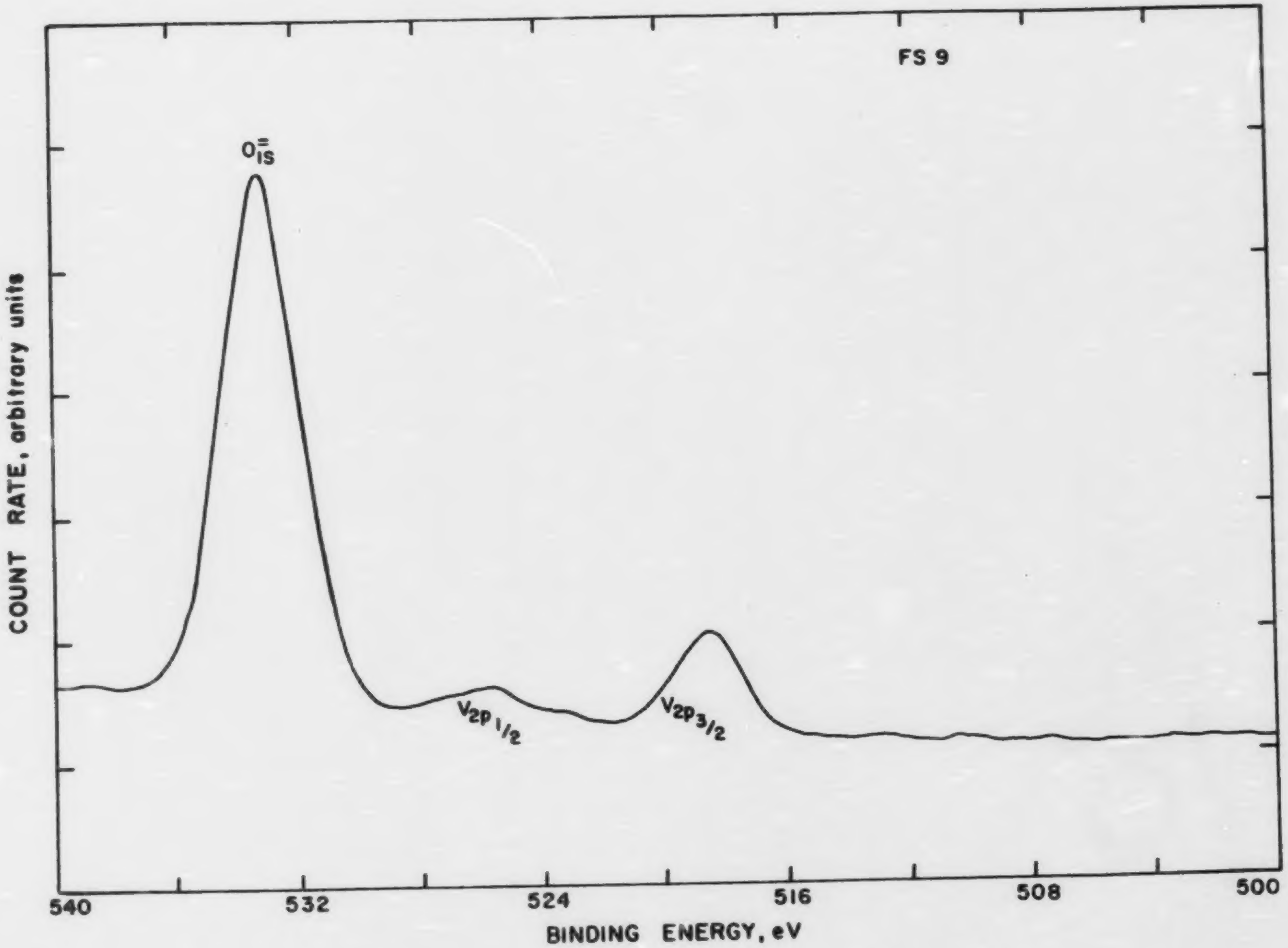

Figure 44. Stack sampling train filter material from bitumen gasification, Run No. 5. Vanadium ESCA scan

V_2O_5, V_2O_3 and VO_2 are present. From an environmental impact perspective, additional specificity is unimportant because all three compounds are equally toxic.[11] However, the surface content of vanadium (1 to 2 percent) is of particular concern in that it is reasonable to assume that surface vanadium compounds on particles embedded in the lung will attack tissue more readily than bulk molecules.

The other element, besides vanadium, of environmental interest is sulfur. Figures 45 and 46 are scans in the sulfur 2p binding energy region. Surface sulfur on the smaller particulate is all bound as sulfate whereas in particulate captured by the cyclone roughly 75 percent is sulfate and 25 percent is sulfide. This difference is not unexpected if it is assumed that a substantial fraction of surface sulfur is formed by reaction in the stack between particulate cations (calcium in this case) and gas phase sulfur dioxide and trioxide.

Gasifier bed, internal cyclone and knockout baffle material - Particulate in these three categories were also analyzed by ESCA. Table 37 contains the results of broadband scans of gasifier bed material (GB9) right hand gasifier cyclone catch (RH9) and stack knockout baffle particulate (KO9).

Table 37. SURFACE CONCENTRATIONS OF GASIFIER BED, GASIFIER CYCLONE AND KNOCKOUT BAFFLE PARTICULATE

Element	Sample, % surface abundance		
	GB9	RH9	KO9
O	47.2	46.8	27.6
Ca	12.9	11.9	6.1
C	38.3	40.0	63.0
S	1.6	1.3	3.0
Na	-	-	0.2

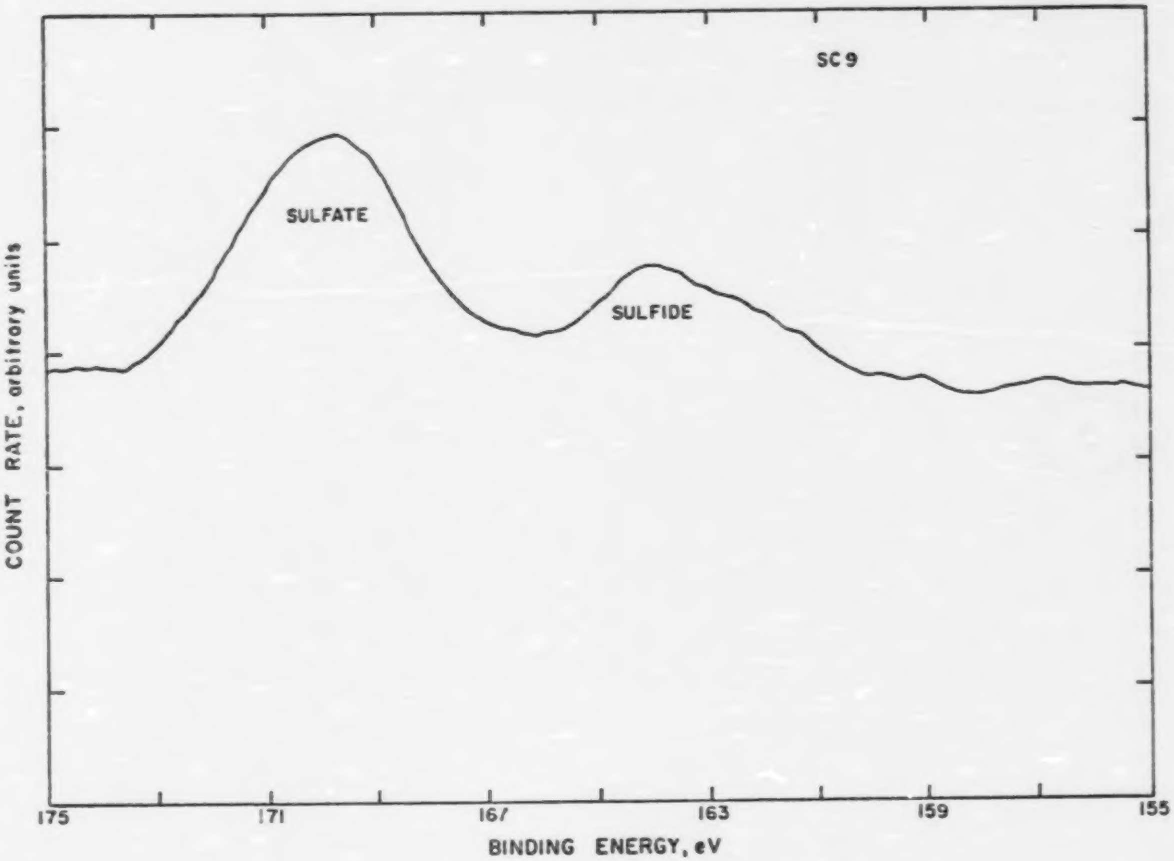

Figure 45. Stack cyclone material from bitumen gasification, Run No. 5. Sulfur ESCA scan

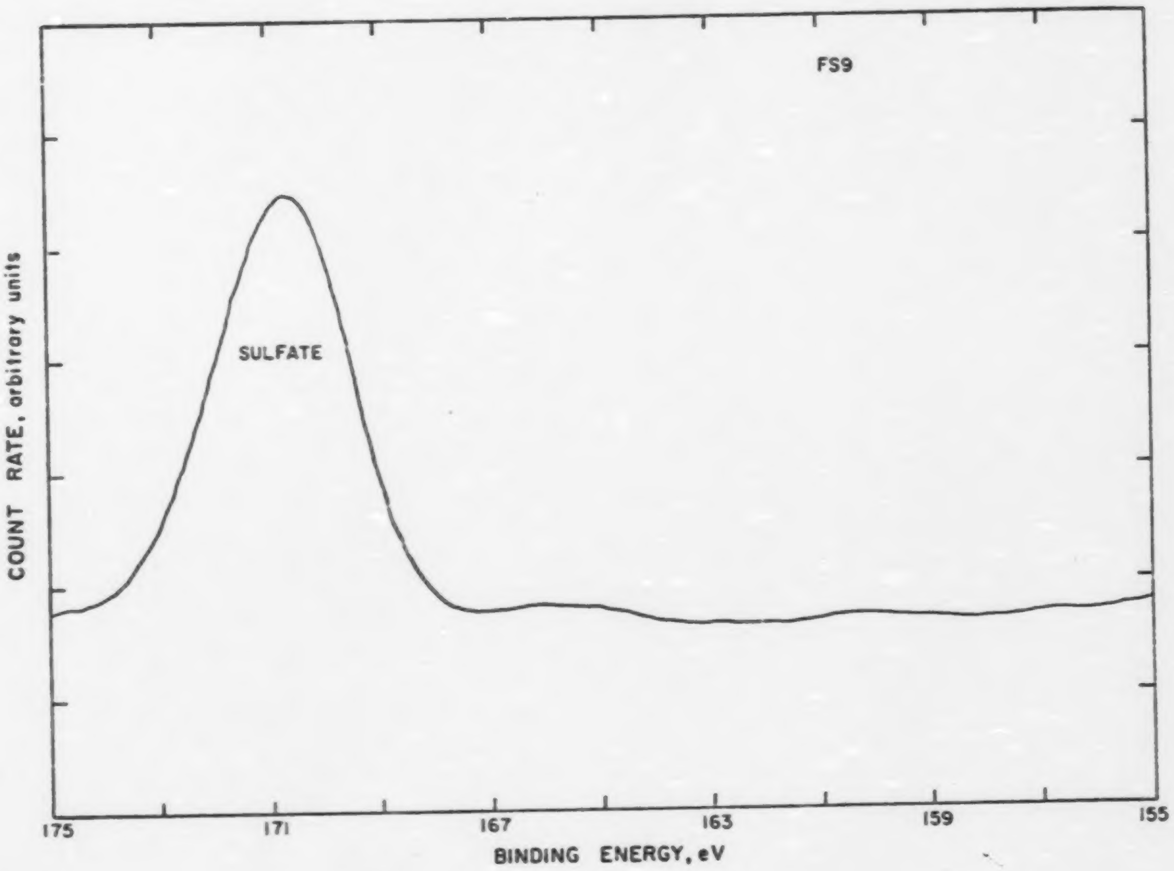

Figure 46. Stack sampling train filter material from bitumen gasification, Run No. 5. Sulfur ESCA scan

Comparison of columns GB9 and RH9 indicates that material captured by the gasifier cyclones is representative of bed material. Knockout baffle particulate is more appropriately compared with material captured by the stack cyclone (SC9). The larger material from the knockout baffle has a somewhat smaller carbon coating, less surface sodium and surface vanadium below 0.2 percent as would be expected from the previous discussion. These findings are similar to those encountered for fuel oil gasification samples.

Spent Stone - Regenerator bed material, representative of CAFB solid waste, from Run 5 was analyzed for organic components, bulk elements and surface elements and compounds. Figures 47 through 54 contain the spectra of organic material extracted from bed stone. Table 38 summarizes the spectral identification and gives the distribution of material among the eight chromatographic fractions. A large variety of compounds are present in the bed material, roughly one-third hydrocarbons and two-thirds oxygenated species. The potential environmental impact of these compounds will depend on the method of disposal and upon the type of predisposal treatment. The effects of leachate containing compounds such as phenols, aromates carbonyls and esters would have to be determined. However, the low abundances of most of the compounds found present coupled with proper disposal does not appear to present any readily apparent deleterious environmental effects.

Bulk elemental analysis of bed material (now shown) indicates that of the major metal elements found in bitumen V, Ni and Na have much lower abundances in this material than in stack particulate. Only iron has the same concentration in both samples. This finding is consistent with the mechanisms proposed earlier for enrichment of V and Na in small particles.

The bulk analysis is confirmed by the ESCA scan shown in Figure 55 which shows neither vanadium nor sodium. Thus the surface abundances of both these elements is less than 0.1 percent in the bed stone.

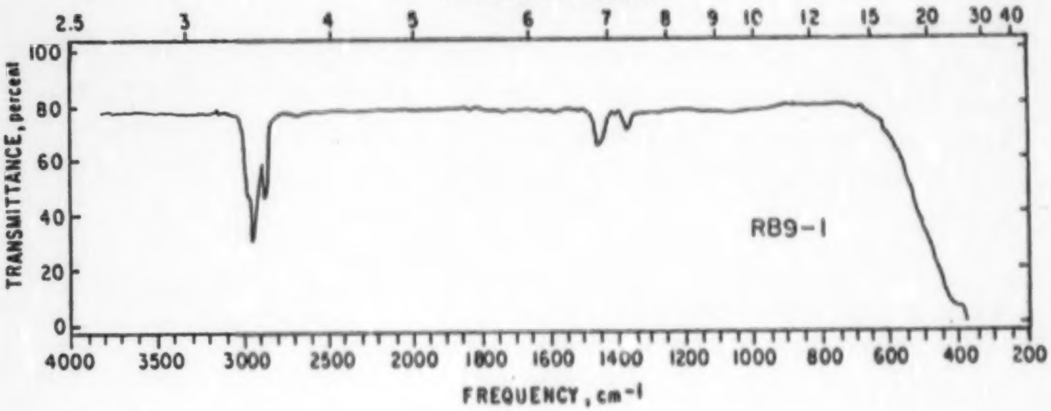

Figure 47. Regenerator bed material from bitumen gasification, Run No. 5, LC fraction 1. Peaks at 2920 cm^{-1} and ~1370 cm^{-1} and 1450 cm^{-1} are from CH_3, CH_2 and indicate aliphatic hydrocarbons

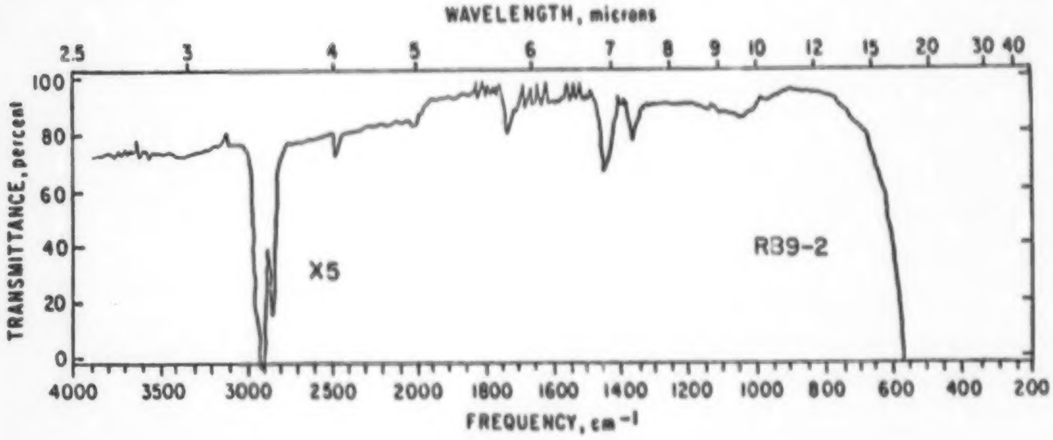

Figure 48. Regenerator bed material from bitumen gasification, Run No. 5, LC fraction 2. See Figure 47

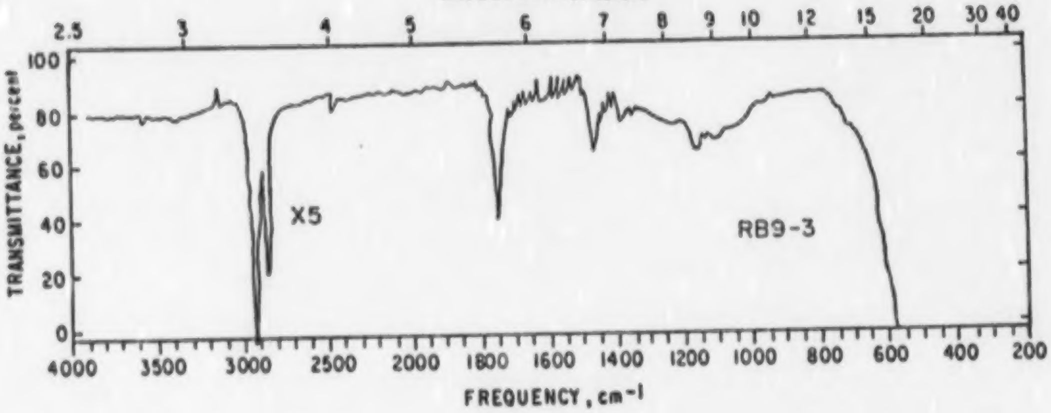

Figure 49. Regenerator bed material from bitumen gasification, Run No. 5, LC fraction 3. See Figure 47. The peak at 1730 cm^{-1} indicates an ester, C=O

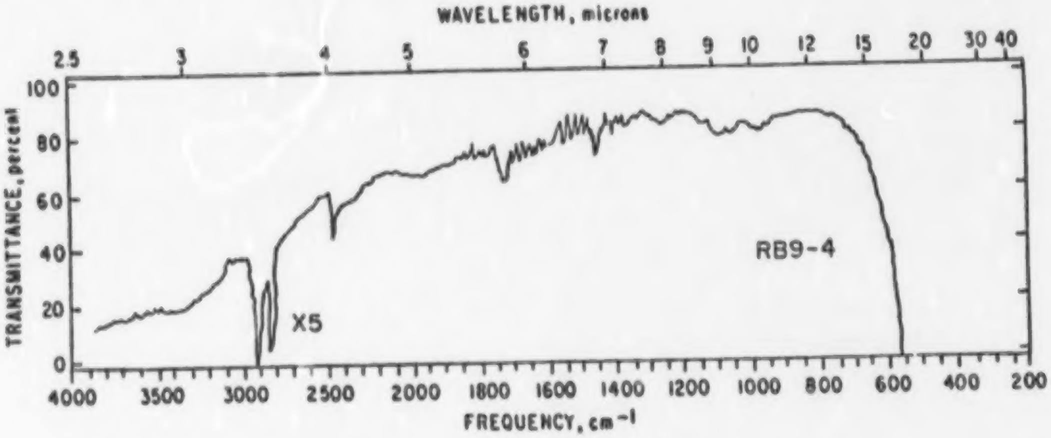

Figure 50. Regenerator bed material from bitumen gasification, Run No. 5, LC fraction 4. See Figure 47. Peak at 1730 cm^{-1} indicates the carbonyl group, C=O. Peak at ~3400 cm^{-1} could be from alcohol or carboxylate

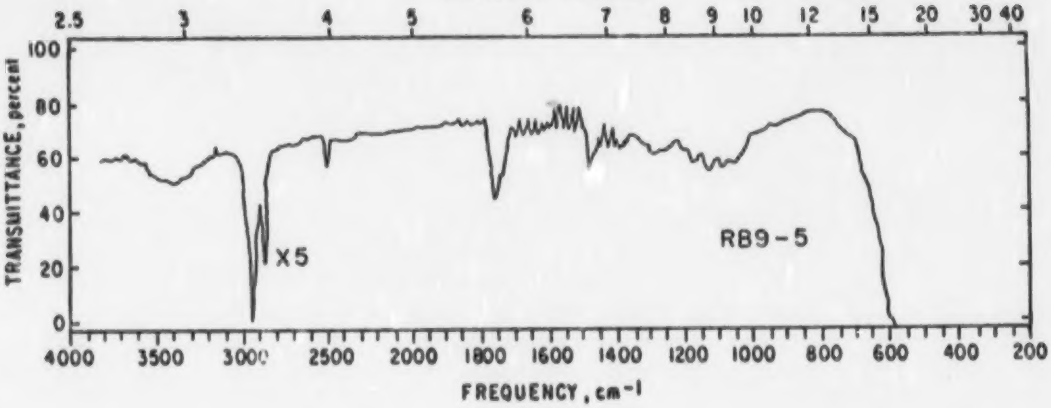

Figure 51. Regenerator bed material from bitumen gasification, Run No. 5, LC fraction 5. See Figure 50

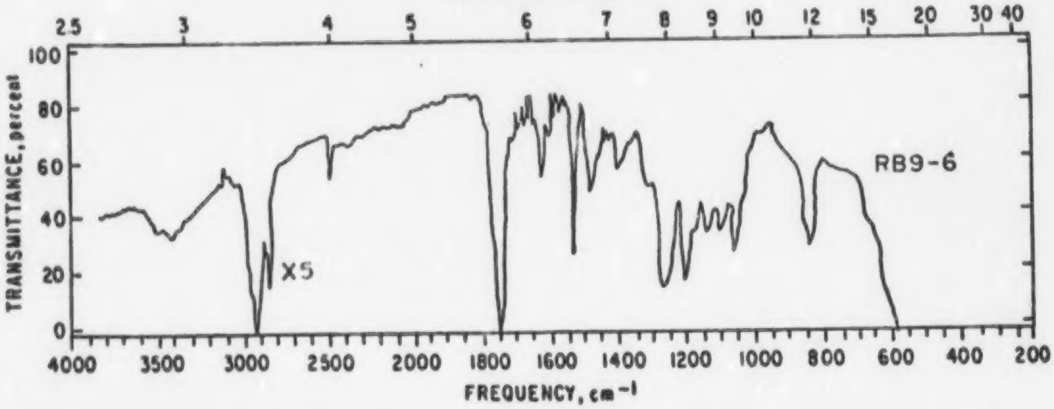

Figure 52. Regenerator bed material from bitumen gasification, Run No. 5, LC fraction 6. Peaks at 2920 cm^{-1} are from CH_3, CH_2 and the peak at 1730 cm^{-1} is from C=0. The peak at 850 cm^{-1} and the number of bands between 1000 and 1600 cm^{-1} suggest the presence of aromatic carbonyl compounds. Peak at 3400 cm^{-1} suggests phenol or carboxylic acids

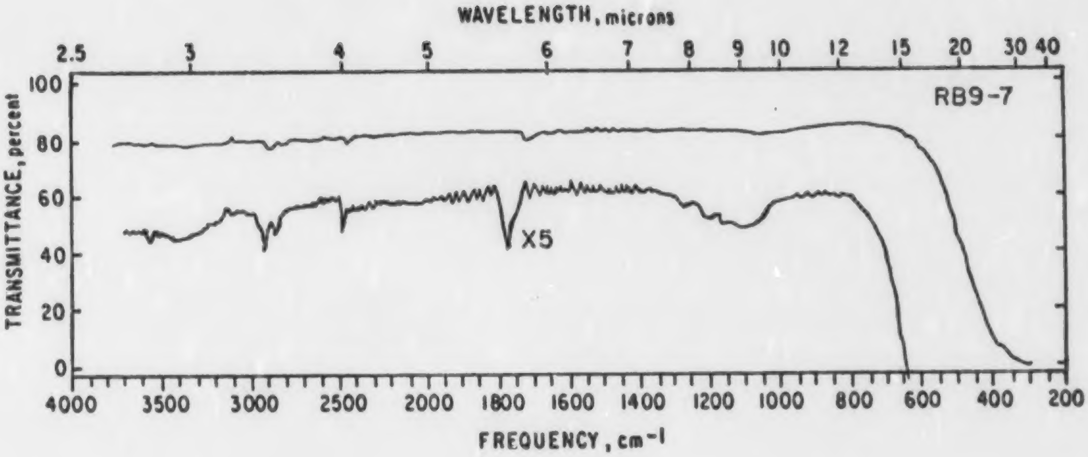

Figure 53. Regenerator bed material from bitumen gasification, Run No. 5, LC fraction 7. Trace quantities of aliphatics and carbonyl compounds may be present

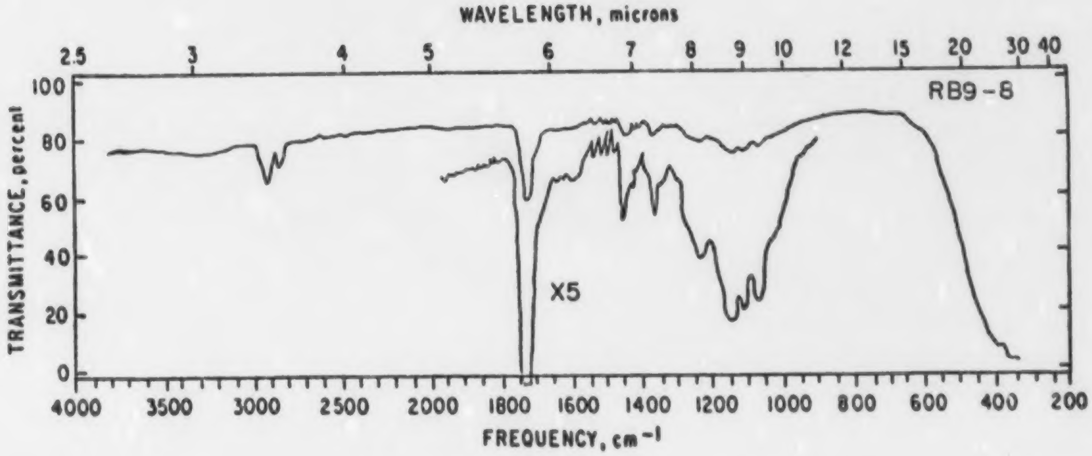

Figure 54. Regenerator bed material from bitumen gasification, Run No. 5, LC fraction 8. See Figure 52

Table 38. DISTRIBUTION OF EXTRACTABLE ORGANIC MATERIAL AND FUNCTIONAL GROUPS IN SPENT STONE: RUN NO. 5

Fraction	Weight, μg	Percentage	Functional groups
1	330	26.9	Aliphatic hydrocarbons
2	64	5.2	Aliphatic hydrocarbons
3	82	6.7	Esters
4	110	9.0	Carboxylate Carbonyls, alcohol
5	85	6.9	As in fraction 4
6	290	23.6	Carbonyls, aromatic carbonyls, phenol, carboxylic acid
7	57	4.6	Carbonyls
8	210	17.1	As in Fraction 6
Total	1,228	100	

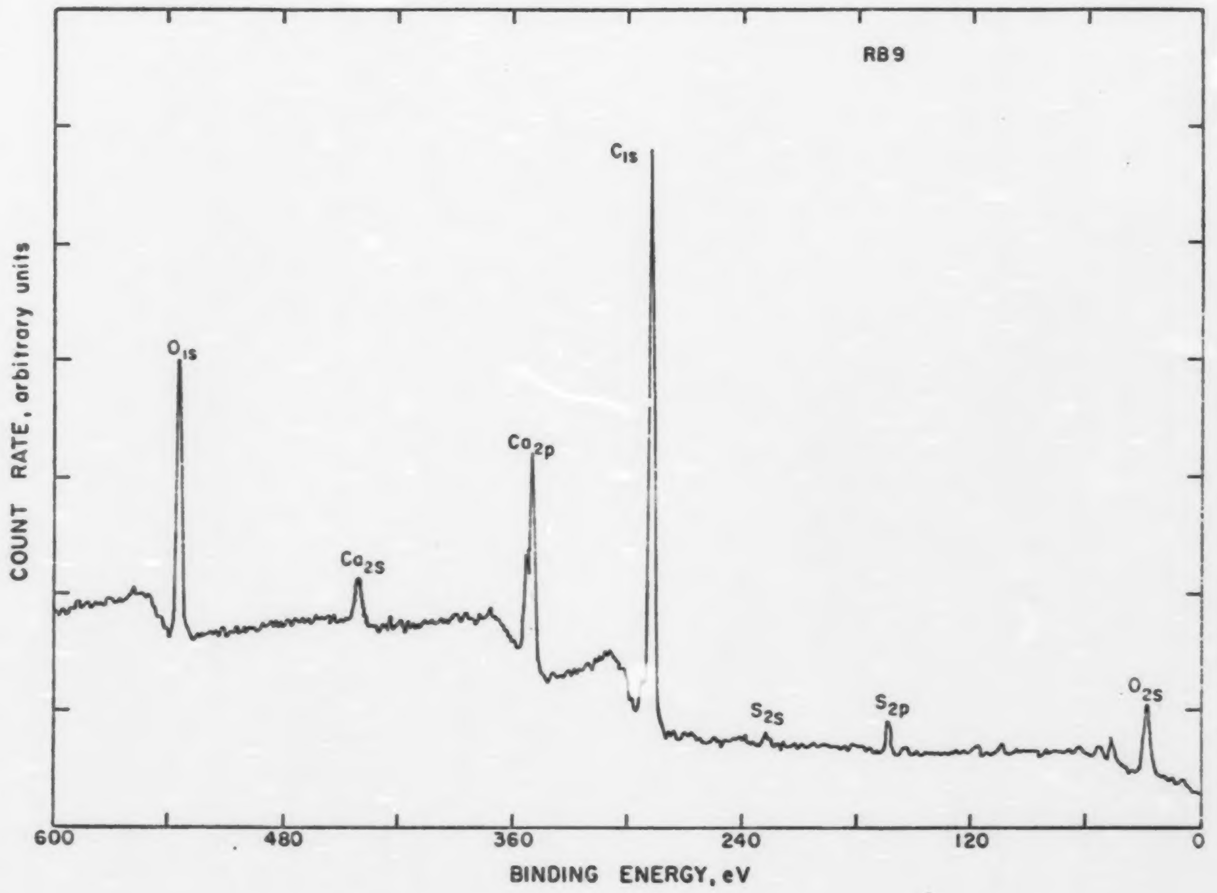

Figure 55. Regenerator bed material from bitumen gasification, Run No. 5. Broadband ESCA scan

Furthermore, scans of spent stone etched to a depth of - 100 Å did not show any vanadium. Surface abundances of the four elements observed on the surface are listed in Table 39. The carbon 1s electron scan presented in Figure 56 shows a substantial concentration of carbonate. This is not unexpected of a material subject to severely oxidizing conditions and is consistent with the substantial carbonyl presence found in the organic analyses and with the finding by ERCA that regenerator bed material is heavily carbon coated.

Table 39. SURFACE CONCENTRATIONS OF SPENT STONE PARTICLES, RUN NO. 5

Element	Abundance, %
O	18.7
C	74.2
Ca	5.1
S	2.0

It is also interesting to note that surface sulfur, shown in Figure 57, is all in the form of sulfide. This is presumably a reflection of the particular conditions of temperature, oxygen feed rate and past history of this stone. Later in this section it is noted that sulfur on spent stone collected during oil gasification during Run 4 is evenly distributed between sulfate and sulfide. Because regenerator bed stone will undergo further treatment before disposal or sale, the state of surface sulfur on stone leaving the regenerator is not directly of environmental importance.

Bitumen Combustion/Start-Up

The only sample available for laboratory analysis during bitumen combustion was the Method 5 filter. Because of the small quantity of particulate collected surface analysis was the only technique employed to characterize

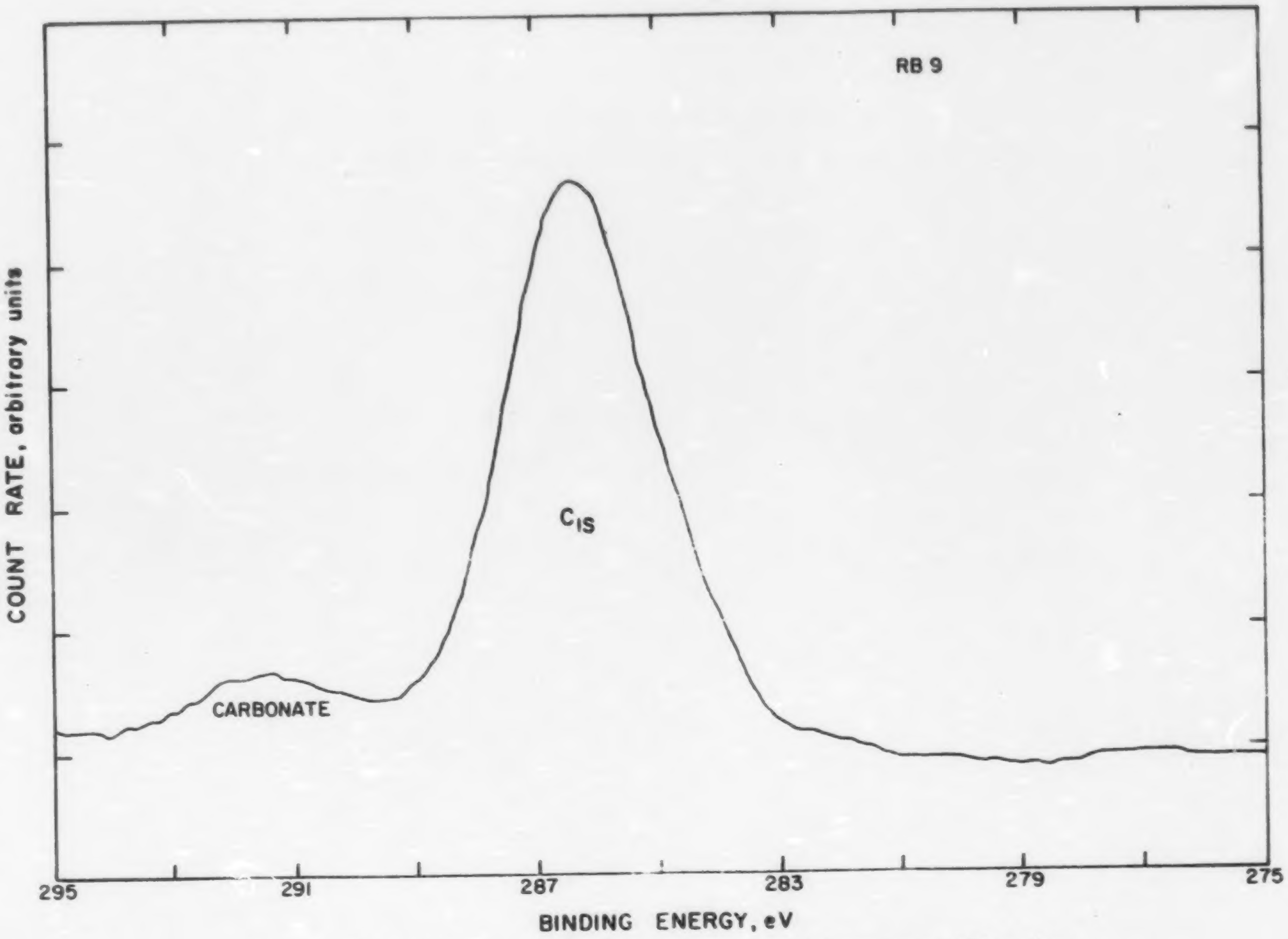

Figure 56. Regenerator bed material from bitumen gasification, Run No. 5. Carbon ESCA scan

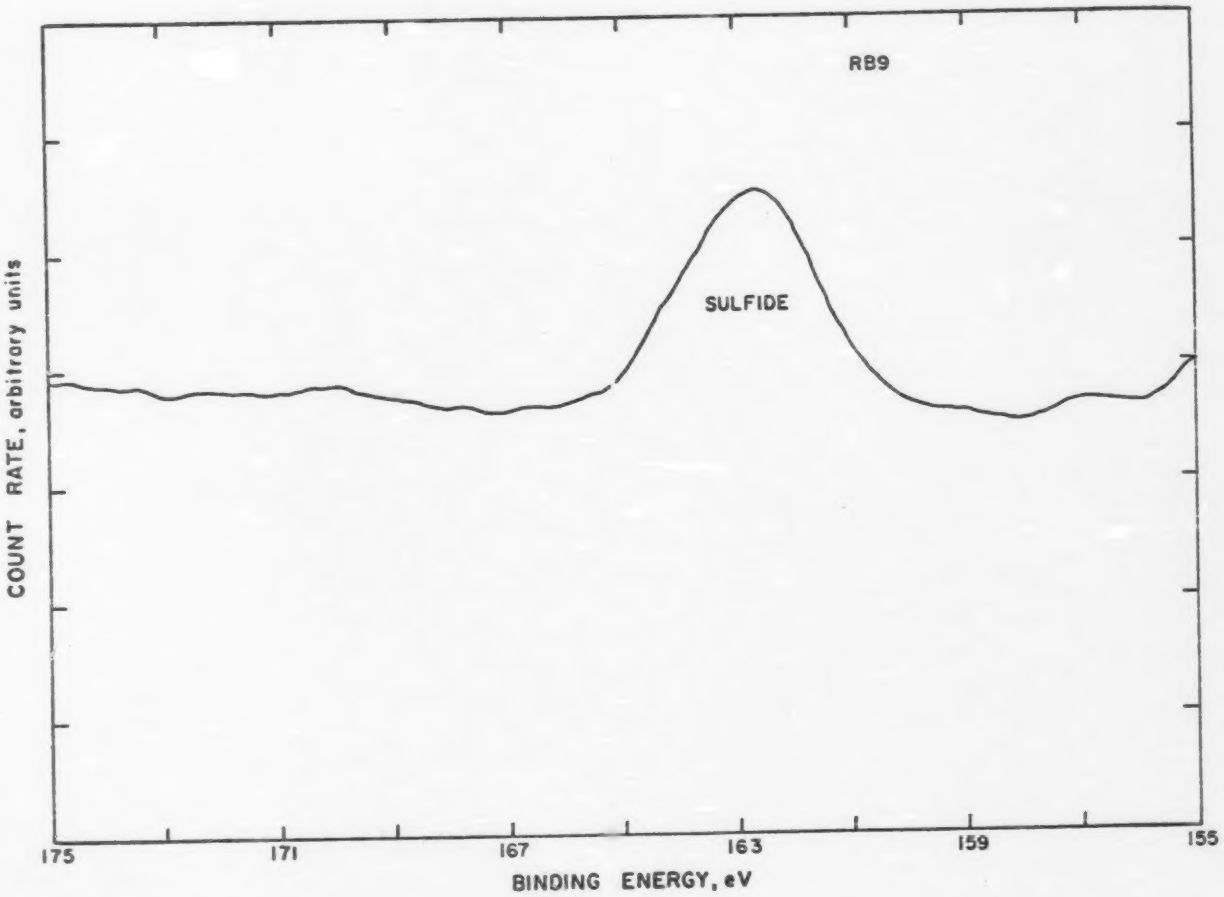

Figure 57. Regenerator bed material from bitumen gasification, Run No. 5. Sulfur ESCA scan

this sample. Figure 58 is a broadband ESCA scan of the stack sampling train filter particulate. Table 40 lists the surface abundance calculated from this scan.

Table 40. SURFACE CONCENTRATIONS OF STACK PARTICULATE RUN NO. 6

Element	Abundance, %
O	40.4
C	49.3
Ca	8.5
Na	1.0
S	1.9

The most striking feature of this spectrum is the absence of vanadium. It may be noted in Tables 26 and 27 that the temperature at the stack sampling port is almost 60°C lower in Run 6 than in Run 5. It can therefore be assumed that the temperature in boiler and cyclones was considerably lower in Run 6. Therefore, vanadium oxide condensation on particulate surfaces occurred well before the stack and was largely covered up by subsequent deposition of other species such as CO_2 reacting with lime to form $CaCO_3$.

Evidence for this explanation is provided in Figure 59 which shows that a substantial portion of surface carbon (~25 percent) is in the form of carbonate. An additional factor contributing to the relatively high proportion of surface carbonate is increased combustion efficiency in the CAFB under conditions of high excess air. Finally, Figure 60 shows that essentially all surface particulate sulfur is bound as sulfate. This is expected under combustion conditions because of the low probability of calcium sulfide formation.

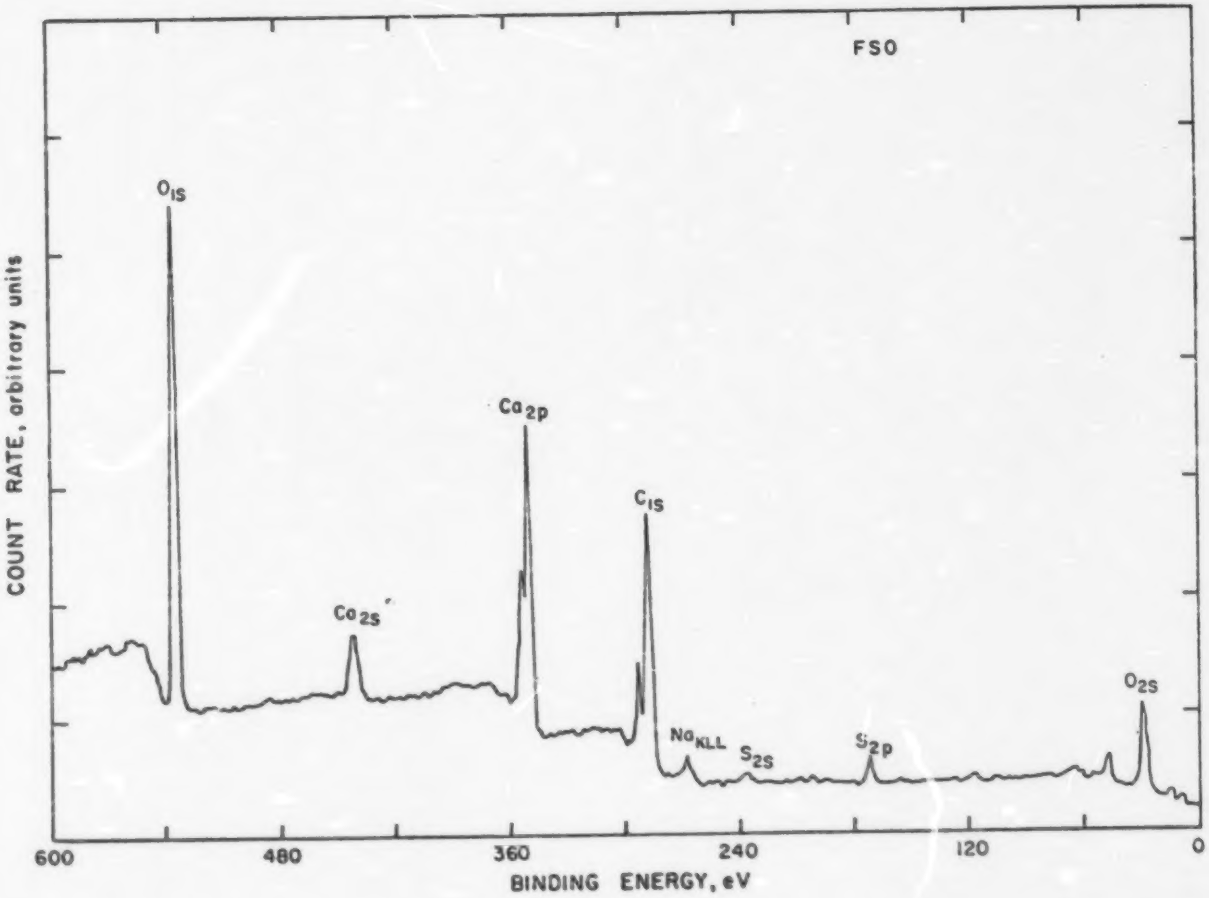

Figure 58. Stack sampling train filter catch during bitumen combustion and fresh limestone feeding, Run No. 6. Broadband ESCA scan

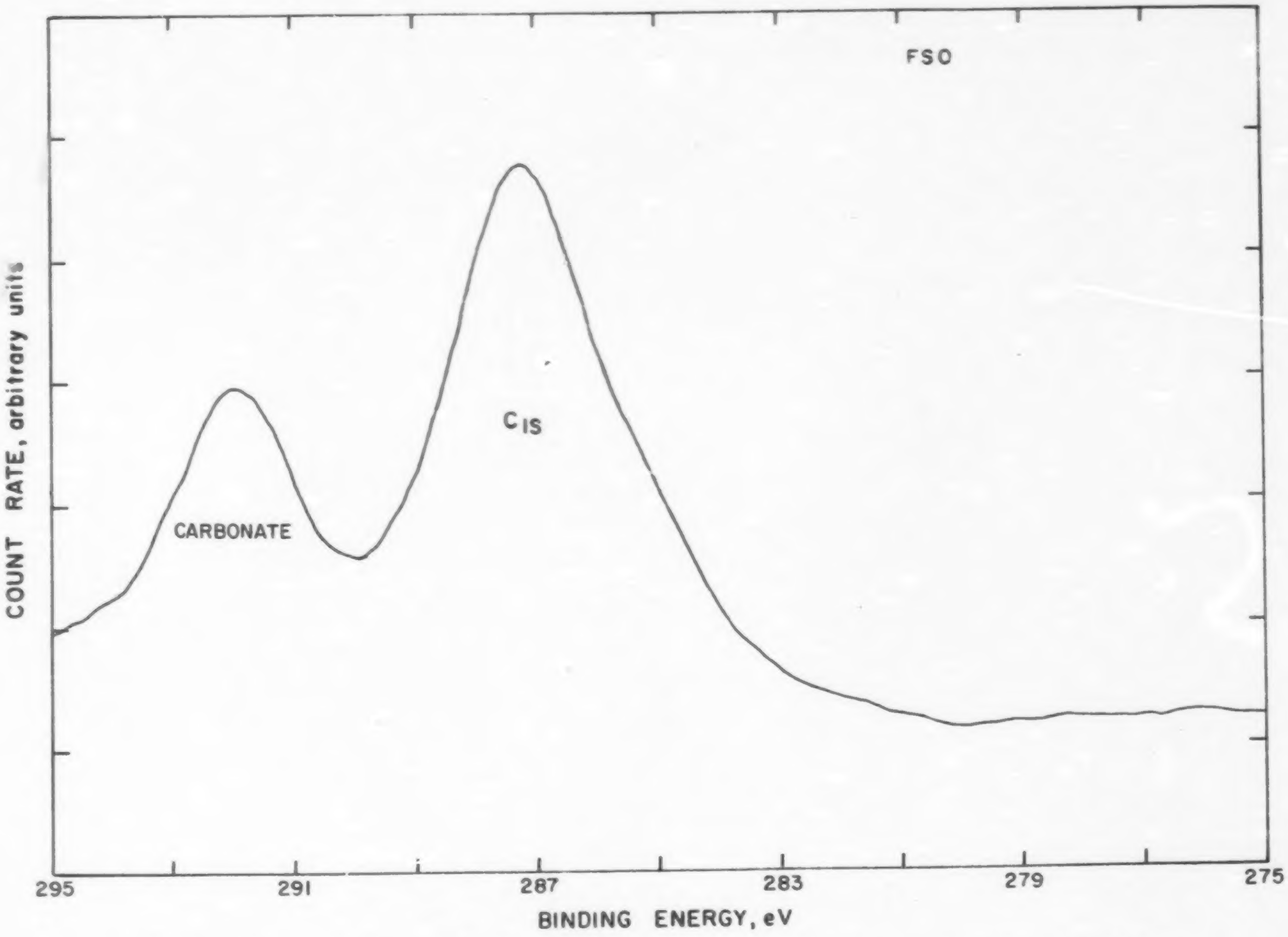

Figure 59. Stack sampling train filter catch during bitumen combustion and fresh limestone feeding, Run No. 6. Carbon ESCA scan

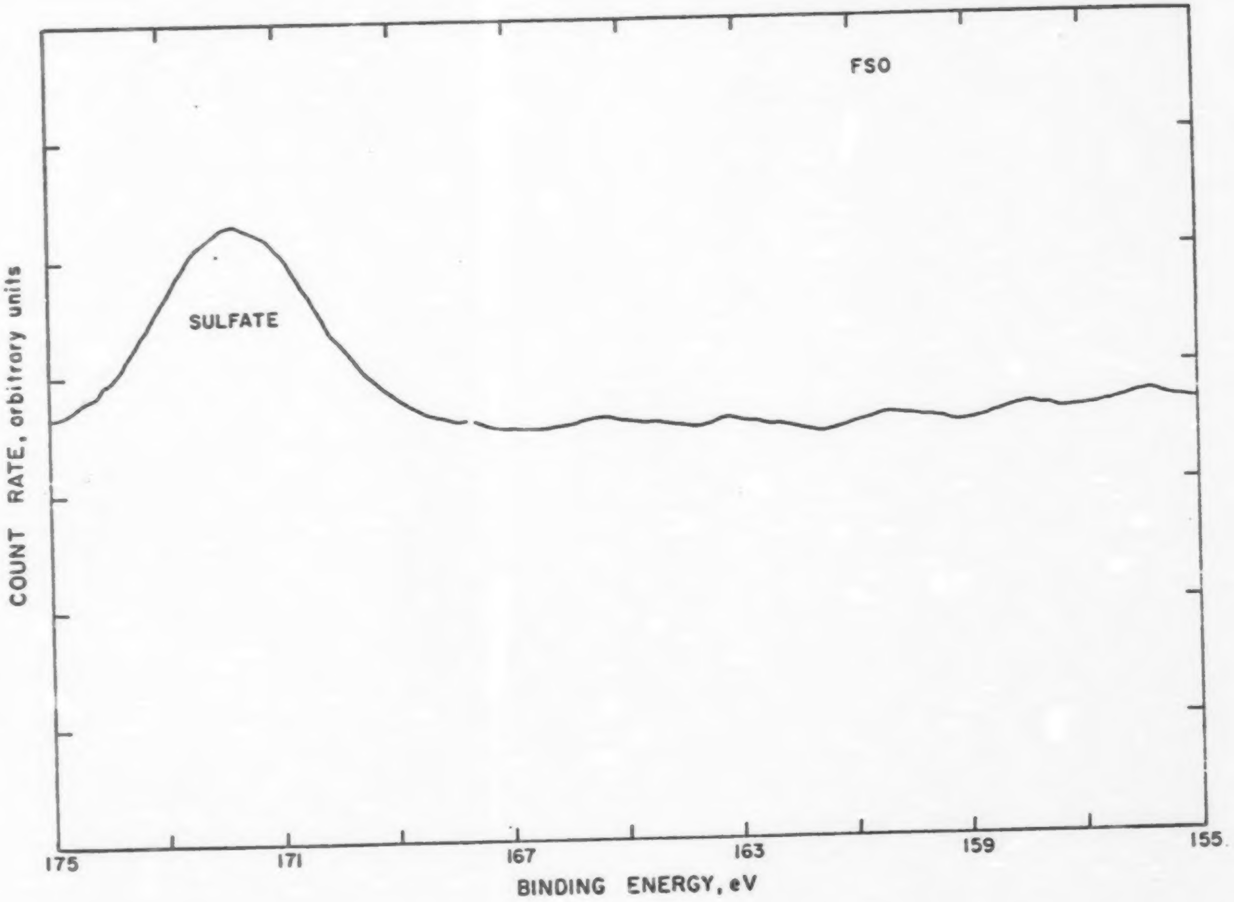

Figure 60. Stack sampling train filter catch during bitumen combustion and fresh limestone feeding, Run No. 6. Sulfur ESCA scan

Fuel Oil Gasification

Stack Particulate - Stack cyclone particles collected during Run 4 were the only samples from fuel oil gasification analyzed for organic functional groups, bulk elemental composition and surface chemicals. In general, the results of the analyses of samples collected during fuel oil gasification are similar to those from bitumen gasification samples.

Figures 61 through 67 contain the infrared spectra of the first seven chromatographic fractions from the extract of stack cyclone particulate. Table 41 summarizes the spectral identifications and presents the weight distribution among the eight fractions. The functional groups identified in this sample and their relative amounts are similar to that found in stack cyclone particulate collected during bitumen gasification (see Table 34). The total condensed organic loading 0.2 mg/m^3 is the same and thus does not appear to represent any significant environmental hazard.

Table 42 contains the results of bulk elemental analysis of the stack cyclone particles. These results are similar to the bitumen stack particulate analysis. The ratios between sulfur, vanadium and nickel in the two sets of particulate are roughly equal to the ratios of those elements in the two fuels. Fluorine is even more abundant in this sample than in the bitumen particulate; the hypotheses advanced in that discussion apply here as well. The substantial chlorine concentration in these particles is unexpected but lower than a worst case analyses prediction based upon the chlorine composition in limestone. As with bitumen emissions, vanadium is the only element of potential concern for the reasons suggested in that discussion.

A number of particulate samples collected during the 4 days of fuel oil combustion were investigated using ESCA. Figure 68 is a broadband scan of stack cyclone particulate (SC8) from Run 4. This spectrum is similar to that of bitumen stack cyclone material (SC9) in Figure 41. Figures 69 through 71 are detailed scans of vanadium, sulfur and carbon. Surface

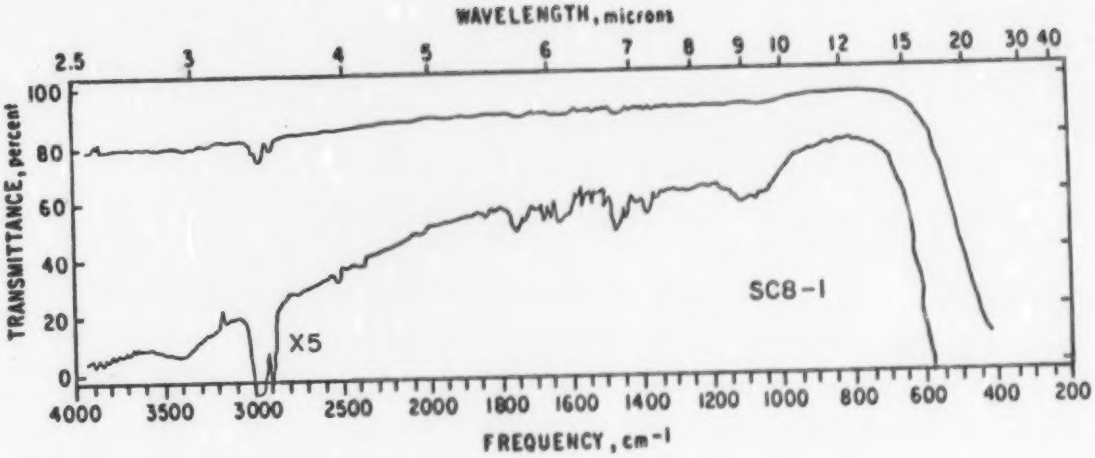

Figure 61. Stack cyclone material from fuel oil gasification, Run No. 4, LC fraction 1. Trace quantities of aliphatic hydrocarbons

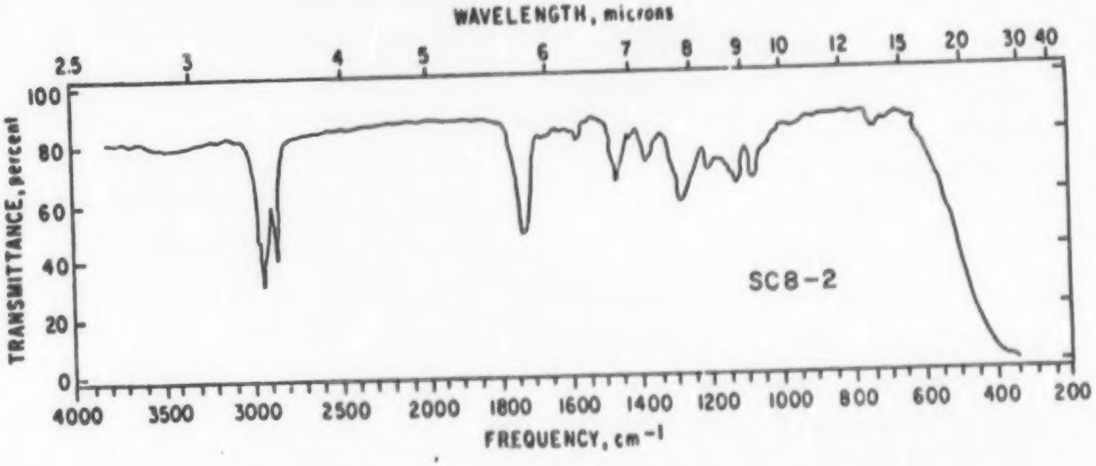

Figure 62. Stack cyclone material from fuel oil gasification, Run No. 4, LC fraction 2. Peak at ~2920 cm^{-1} and peaks at 1450 cm^{-1} and 1370 cm^{-1} are from CH_3, CH_2, while the peak at 1730 cm^{-1} indicates the carbonyl group C=O. This suggests the presence of aliphatic esters. Peaks between 1100 cm^{-1} and 1500 cm^{-1} indicate presence of other C=O containing species

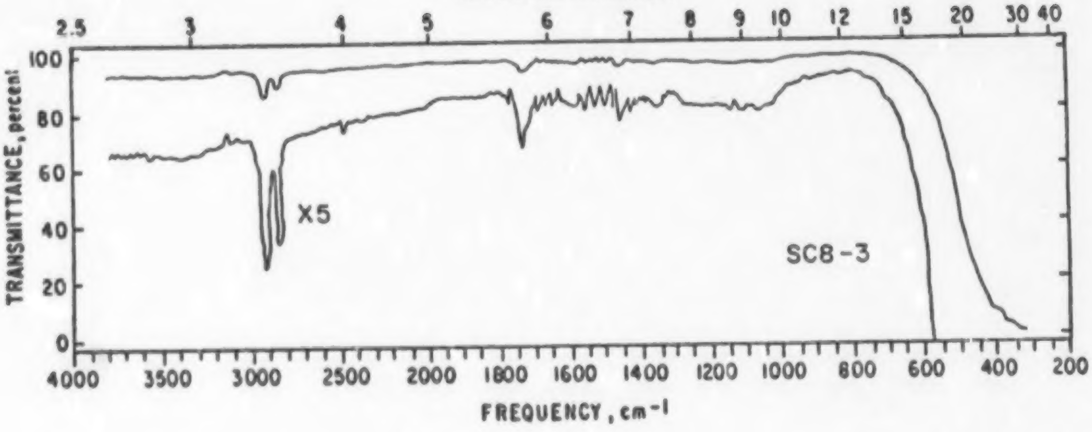

Figure 63. Stack cyclone material from fuel oil gasification, Run No. 4, LC fraction 3. Peaks at ~2920 cm^{-1} and ~1730 cm^{-1} indicate presence of aliphatic ester

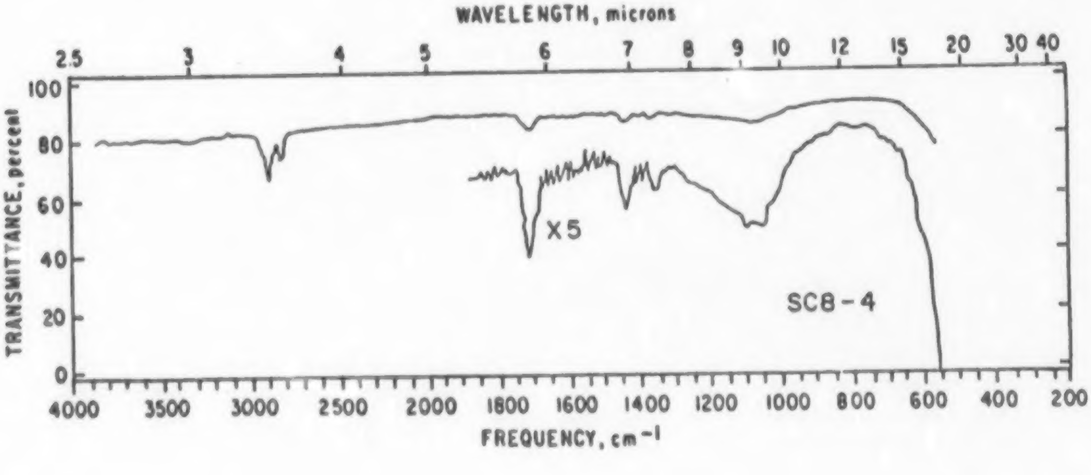

Figure 64. Stack cyclone material from fuel oil gasification, Run No. 4, LC fraction 4. Peak at ~2920 cm^{-1} and peaks at 1450 cm^{-1} and 1370 cm^{-1} indicate aliphatics, while peak at 1730 cm^{-1} indicates C=O. Sample probably contains aliphatic esters, ketones, or aldehydes. Broad band between 1000-1100 cm^{-1} probably comes from SiO_2 impurity

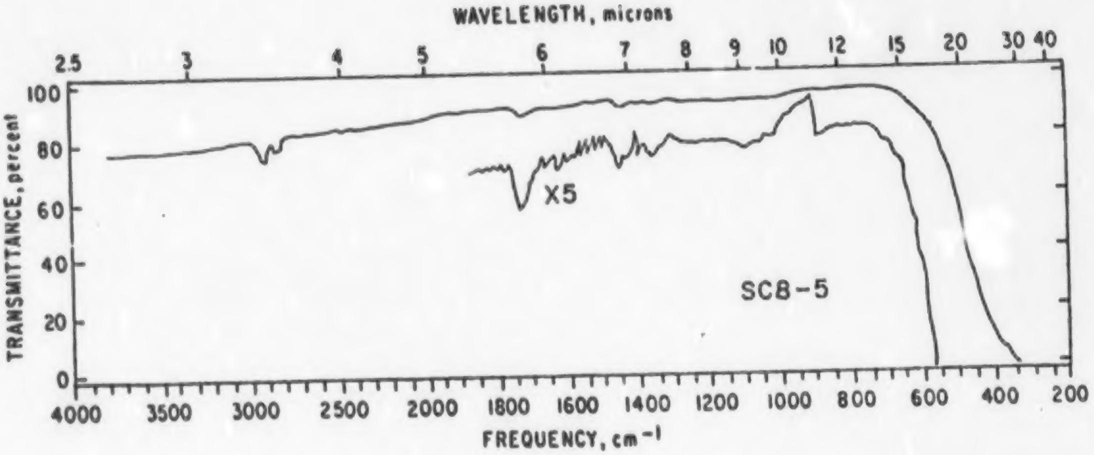

Figure 65. Stack cyclone material from fuel oil gasification, Run No. 4, LC fraction 5. Presence of carbonyl compounds suggested by structure 1730 cm^{-1}

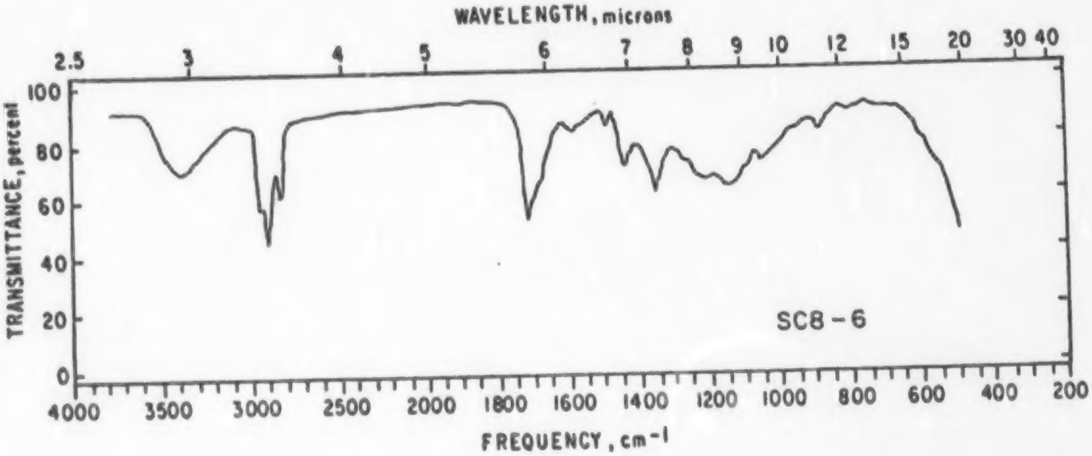

Figure 66. Stack cyclone material from fuel oil gasification, Run No. 4, LC fraction 6. Peaks at ~2920 cm^{-1}, 1450 cm^{-1}, and 1370 cm^{-1} indicate aliphatic esters. Peaks at ~3400 cm^{-1} and between 1100-1300 cm^{-1} suggest presence of carboxylates or alcohols

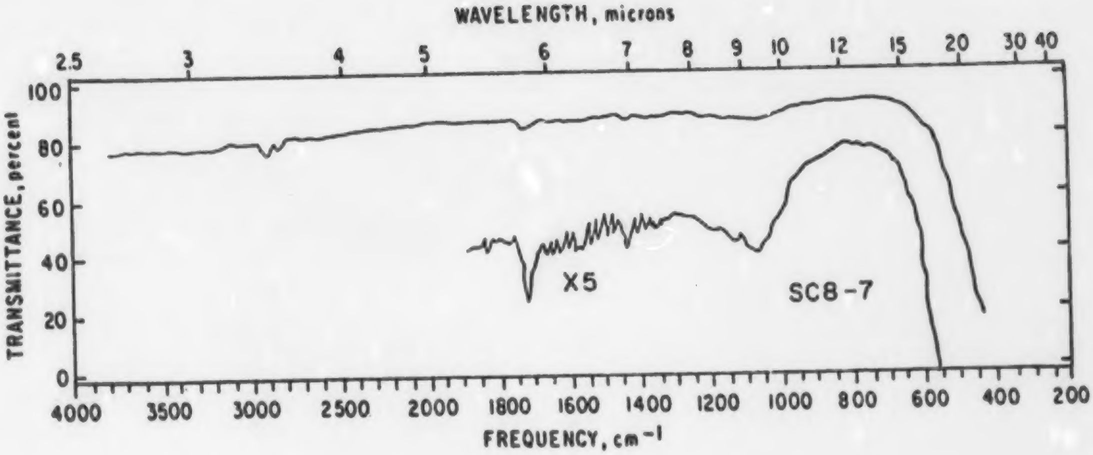

Figure 67. Stack cyclone material from fuel oil gasification, Run No. 4, LC fraction 7. Peak at 1730 cm^{-1} suggests mixture of carbonyl compounds. Broad band between 1000-1100 cm^{-1} probably from SiO_2 impurity

Table 41. DISTRIBUTION OF EXTRACTABLE ORGANIC MATERIAL AND FUNCTIONAL GROUPS IN STACK CYCLONE PARTICULATE: RUN NO. 4

Fraction	Weight, μg	Percentage	Functional groups
1	97	11.2	Aliphatic hydrocarbons,
2	210	24.1	carbonyls, aliphatic esters, C=0 contain species
3	28	3.2	Aliphatic esters,
4	120	13.8	C=0 species, aliphatic esters, ketones, aldehydes
5	180	20.7	Carbonyls
6	200	23.0	aliphatic esters, carboxylates, alcohols
7	35	4.0	Carbonyls
8	0	0	—
Total	870	100	

Table 42. MASS SPECTROGRAPHIC AND ATOMIC ABSORPTION SPECTROMETRIC ANALYSIS OF STACK CYCLONE PARTICULATE: RUN NO. 4

Element[a]	Concentration, ppmw or percent
Ca[c]	34.5 %
S[b]	2.13
V[c]	0.80
Mg	0.32
Si	0.21
Cl	0.16
Fe[c]	0.15
F	0.13
Al	0.13
Ni[c]	0.10
Na	850 ppmw
K	340
Sr	180
Ba	150
Ti	150
P	96
Zn	80
Br	60
Mn	50
Pb	47
Cu	44
Cr	31
Mo	14
B	5.0
Co	5.0
Zr	3.0
I	2.9
Li	2.1

Table 42 (continued). MASS SPECTROGRAPHIC AND ATOMIC ABSORPTION SPECTROMETRIC ANALYSIS OF STACK CYCLONE PARTICULATE: RUN NO. 4

Element[a]	Concentration, ppmw or percent
Se	1.3ppmw
W	1.1
Sn	1.0
Ce	1.0
Cd	0.8
La	0.8
Ge	0.6
Y	0.5
Rb	0.5
Yb	<0.5
Ga	0.4
Ta	0.4
Bi	<0.3
Hf	<0.3
Nb	0.2
Nd	0.2
Dy	0.2
Sm	<0.2
Th	<0.2
Be	<0.12
Pr	0.1
Tl	<0.1

[a] Elements not listed are <0.1 ppm, not detected.

[b] Determined by wet chemistry.

[c] Determined by atomic absorption spectrometry.

[d] Used as internal standard.

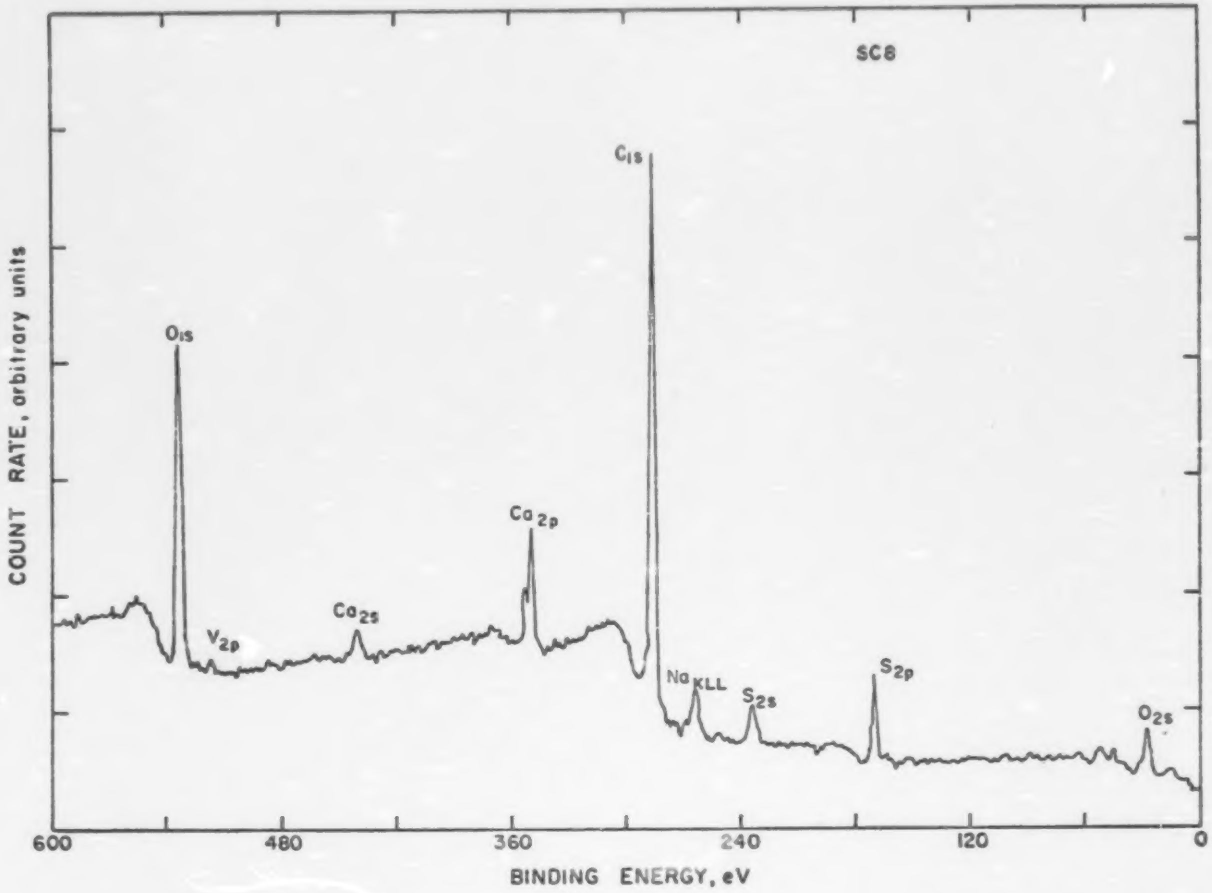

Figure 68. Stack cyclone material from fuel oil gasification, Run No. 4. Broadband ESCA scan

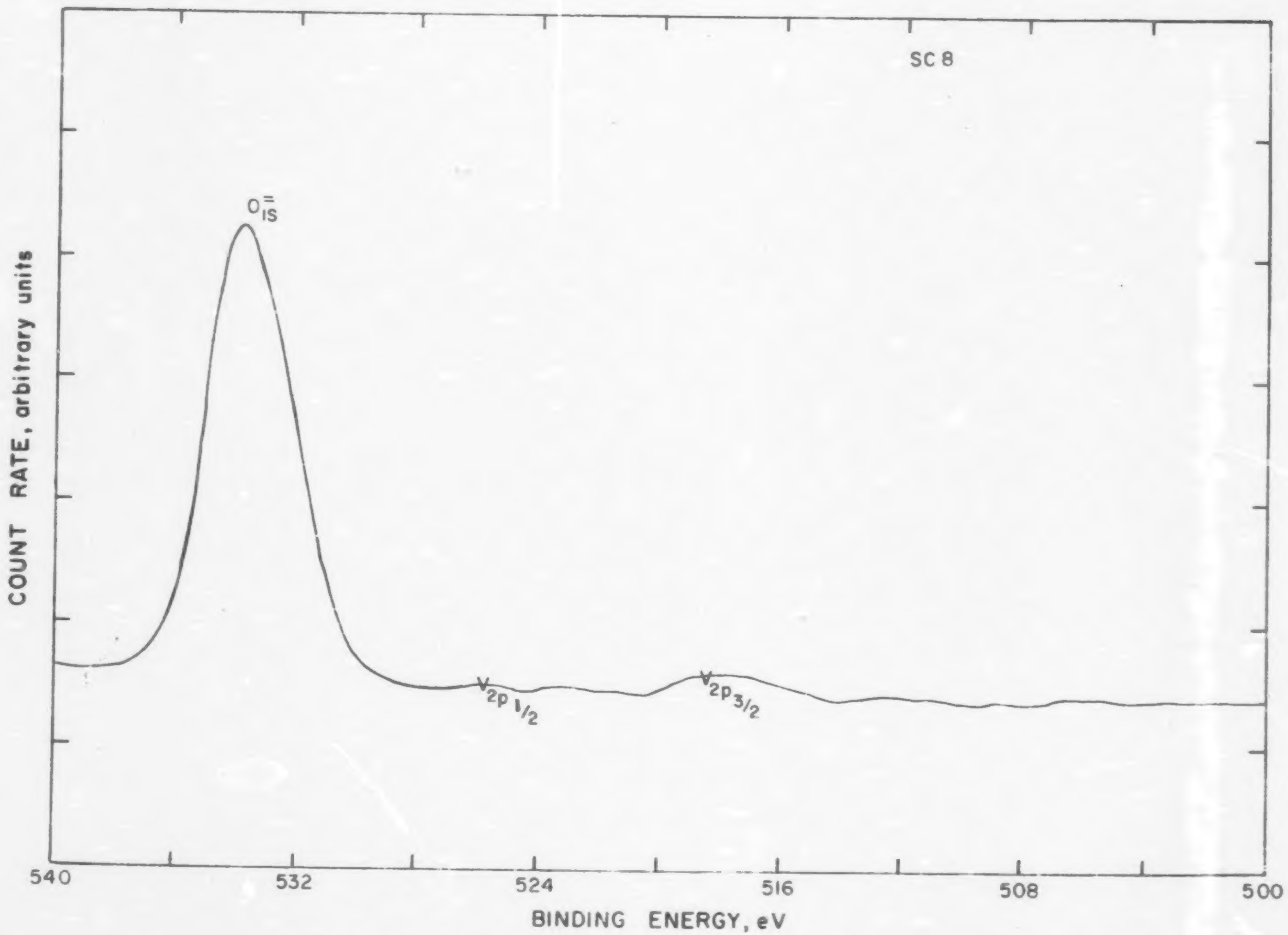

Figure 69. Stack cyclone material from fuel oil gasification, Run No. 4. Vanadium ESCA scan

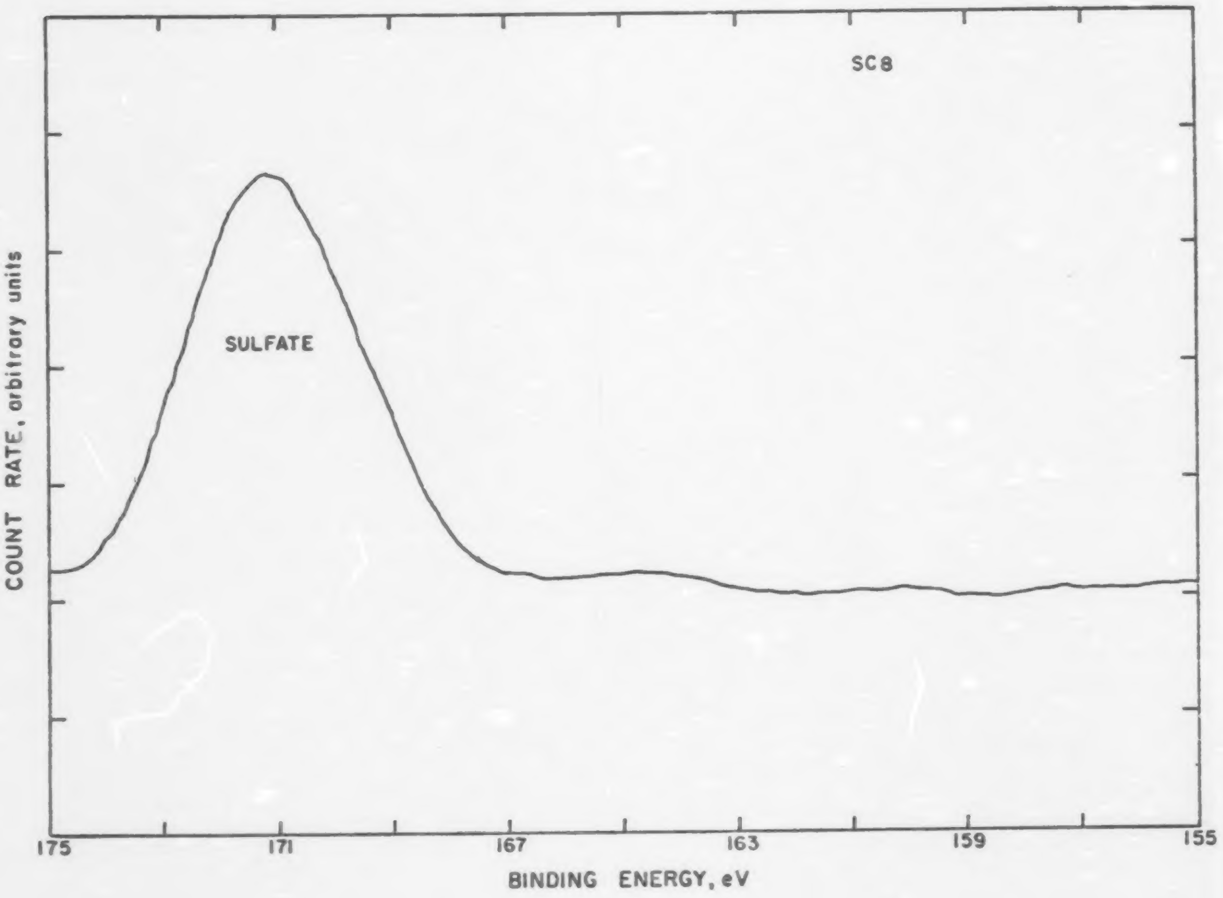

Figure 70. Stack cyclone material from fuel oil gasification, Run No. 4. Sulfur ESCA scan

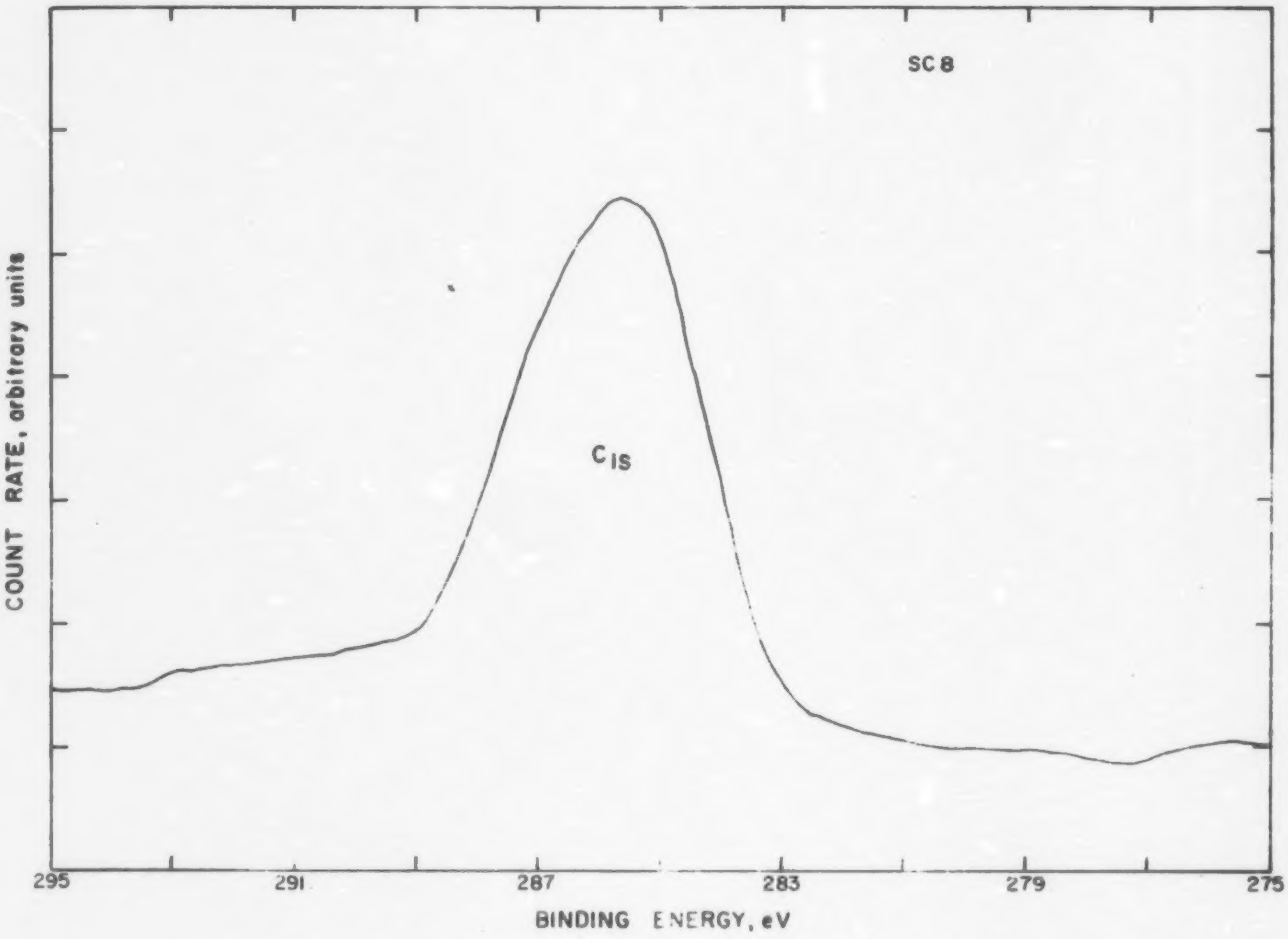

Figure 71. Stack cyclone material from fuel oil gasification, Run No. 4. Carbon ESCA scan

vanadium is, as was the case during bitumen gasification, present in a mixture of oxides. Sulfur is all in the form of sulfate, reflecting the large quantity of excess oxygen (5.3 percent) in the flue gas. The carbon 1s spectrum is asymmetric toward the higher binding energy region reflecting the high proportion of oxygenated organic species found by the organic analysis.

Broadband scans of particulate captured by the filter in Runs 1 to 4 were also taken. Figures 72 and 73 are broadband surface and subsurface spectra of filter particulate collected during Run 4. Spectra of samples from Runs 1 to 3 are not shown but are summarized in Table 43. Surface and subsurface elemental compositions in Runs 1, 2 and 4 are remarkably similar. The filter catch in Run 3 has a substantially larger carbon abundance which, in fact, increases slightly from the surface to a depth of ~ 100 Å. This anomalous behavior does not correlate to any other emission properties measured during Run 3.

Table 44 lists the elemental abundances found on particulate collected by the impactor. As was the case with bitumen samples, impactor particulate is more heavily carbon coated than particulate collected on the hi-vol sampling train filter. This may be merely a reflection of the heavier carbon coating on the pure aluminum substrates than on the filter material (see Figures 13 and 14), since impactor substrate coverage is light. The appearance of silicon on several of the substrates is most likely due to left over silicon grease from early impactor runs. The most surprising observations are the lack of any detectable vanadium, even on the subsurface scans and the relatively small quantities of sulfur and sodium. Taken together, these results suggest that substantial deposition of carbonaceous material occurs in the impactor as the flue gas cools

Spent Stone - The only analyses of regenerator bed material are the surface spectra shown in Figures 74 through 76. Relative surface element abundances listed in Table 45 are identical to those found in bitumen spent stone. The carbonate/organic carbon ratios are also the same. The

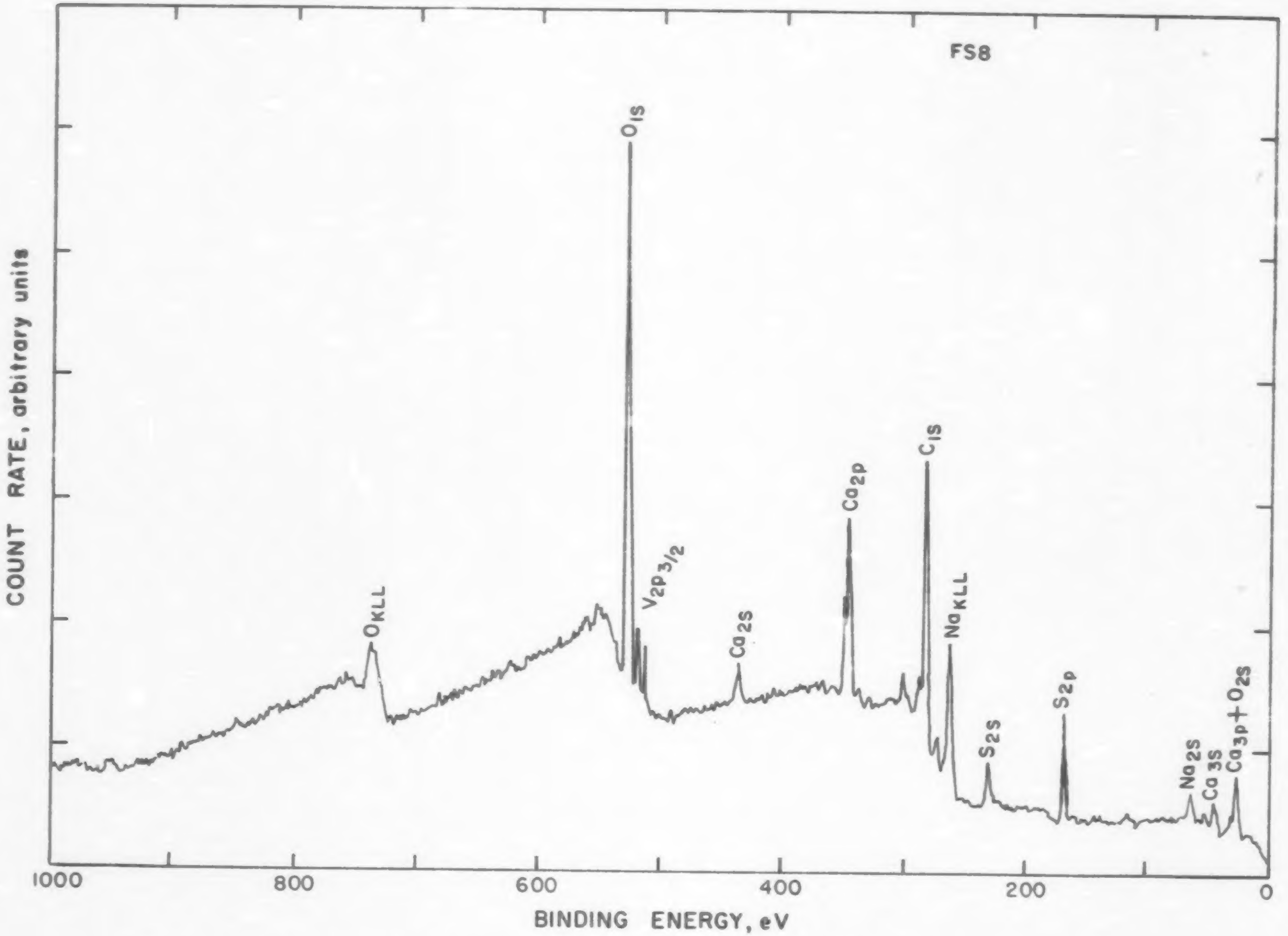

Figure 72. Stack sampling train filter material from fuel oil gasification, Run No. 4. Surface broadband ESCA scan

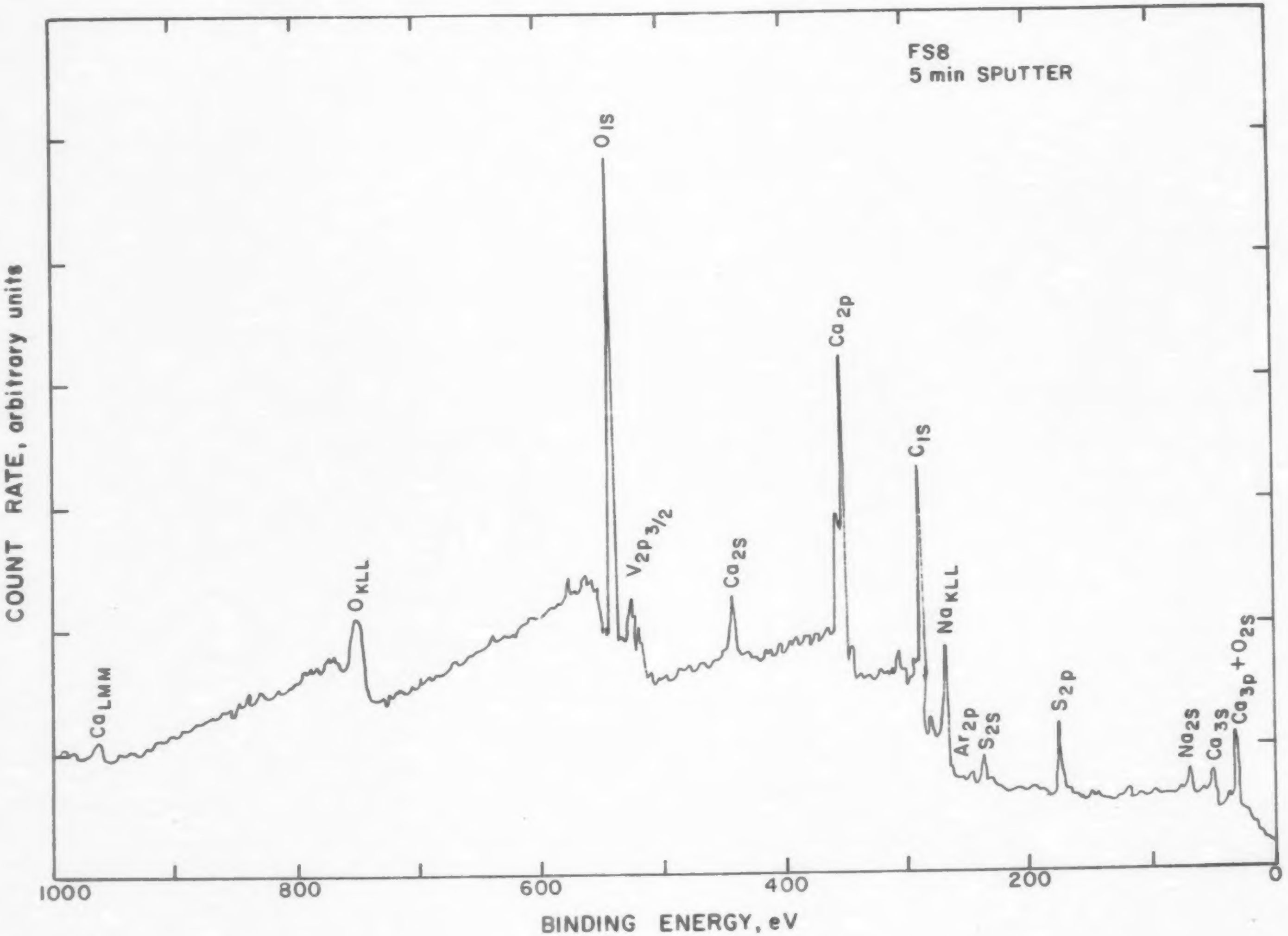

Figure 73. Stack sampling train filter material from fuel oil gasification, Run No. 4. Subsurface broadband ESCA scan

Table 43. SURFACE AND SUBSURFACE CONCENTRATIONS OF STACK PARTICULATE COLLECTED DURING FUEL OIL GASIFICATION: RUNS 1 TO 4

	Sample, % abundance								
	SC8[a]	FS8[a]		FS6[b]		FS5[c]		FS4[d]	
Element	Surface	Surface	Sub-surface	Surface	Sub-surface	Surface	Sub-surface	Surface	Sub-surface
O	22.2	39.8	38.9	19.3	12.4	43.2	47.7	41.1	44.5
V	0.4	1.7	1.6	0.9	0.8	1.6	1.2	0.6	0.3
Ca	2.9	4.7	8.5	0.8	1.8	6.1	9.9	5.3	10.4
C	68.0	43.3	42.3	70.8	79.8	37.2	30.2	40.5	36.6
Na	1.0	3.3	2.5	2.1	1.6	3.1	3.9	2.5	1.6
S	5.4	7.2	6.2	4.5	3.6	8.9	8.2	8.3	4.5
F	-	-	-	0.8	-	-	-	1.7	1.2
Cℓ	-	-	-	-	-	-	0	-	0.9
N	-	-	-	0.9	-	-	-	-	-

[a] Run 4.
[b] Run 3.
[c] Run 2.
[d] Run 1.

Table 44. SURFACE AND SUBSURFACE CONCENTRATIONS OF PARTICULATE COLLECTED ON IMPACTOR SUBSTRATES: RUN NO. 4

	Sample, % abundance									
	UW61	UW62	UW63		UW64	UW65	UW66		UW67	UW68
Element	Surface	Surface	Surface	Sub-surface	Surface	Surface	Surface	Sub-surface	Surface	Surface
O	22.4	20.5	25.2	70.4	24.8	22.7	33.9	39.2	25.9	10.8
Ca	-	-	0.6	1.7	0.3	-	-	-	-	-
C	72.6	75.8	69.3	24.0	70.2	73.7	60.8	58.6	69.1	85.4
Na	0.8	0.4	0.9	0.9	0.9	0.6	0.9	0.7	0.2	1.2
S	1.6	1.4	1.6	2.2	1.1	1.1	2.1	1.5	1.1	2.1
N	1.5	-	1.3	-	1.9	0.9	1.8	-	1.3	-
F	-	-	0.3	-	-	-	0.5	-	-	-
Si	1.1	1.9	0.7	-	-	1.0	-	-	1.3	-
Cℓ	-	-	-	0.8	1.0	-	-	-	0.6	-
V	-	-	-	-	-	-	-	-	-	0.4

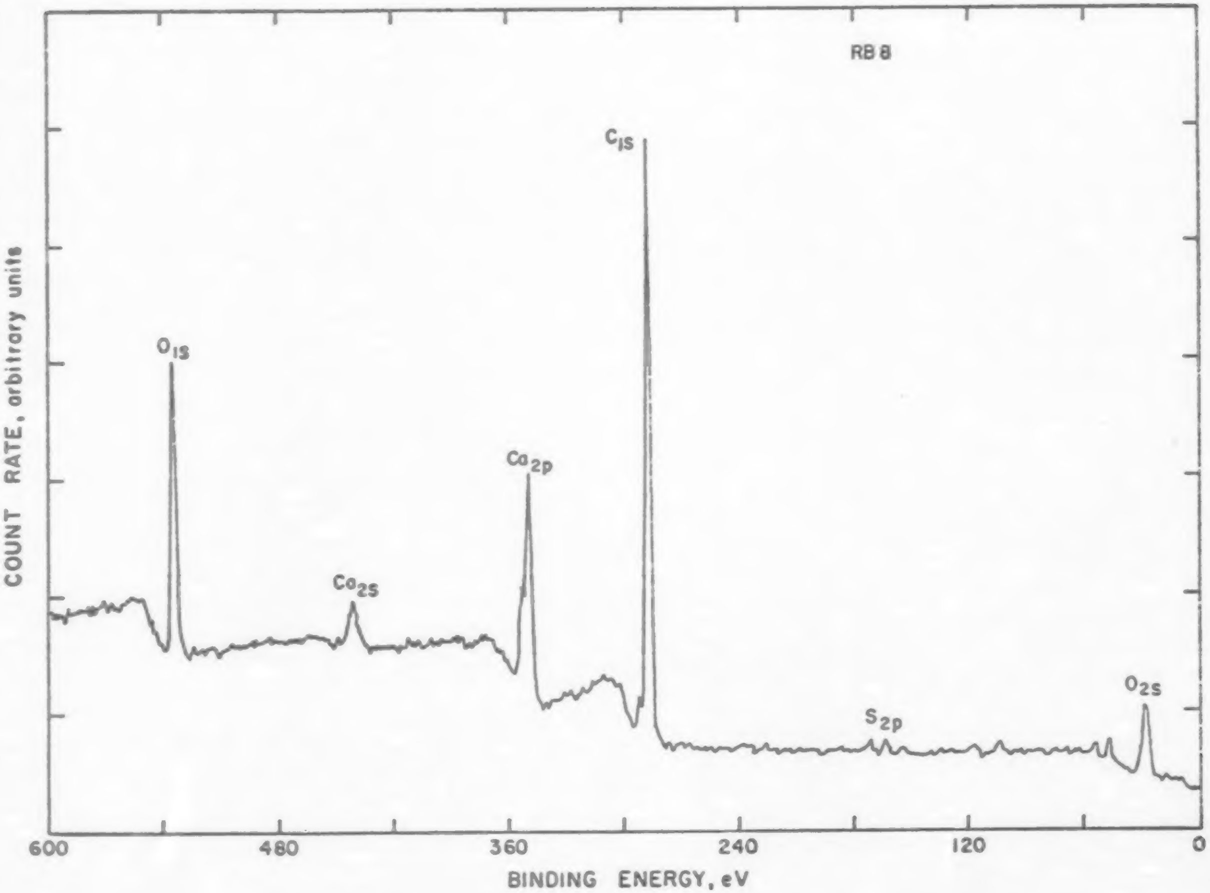

Figure 74. Regenerator bed material from fuel oil gasification, Run No. 4. Broadband ESCA scan

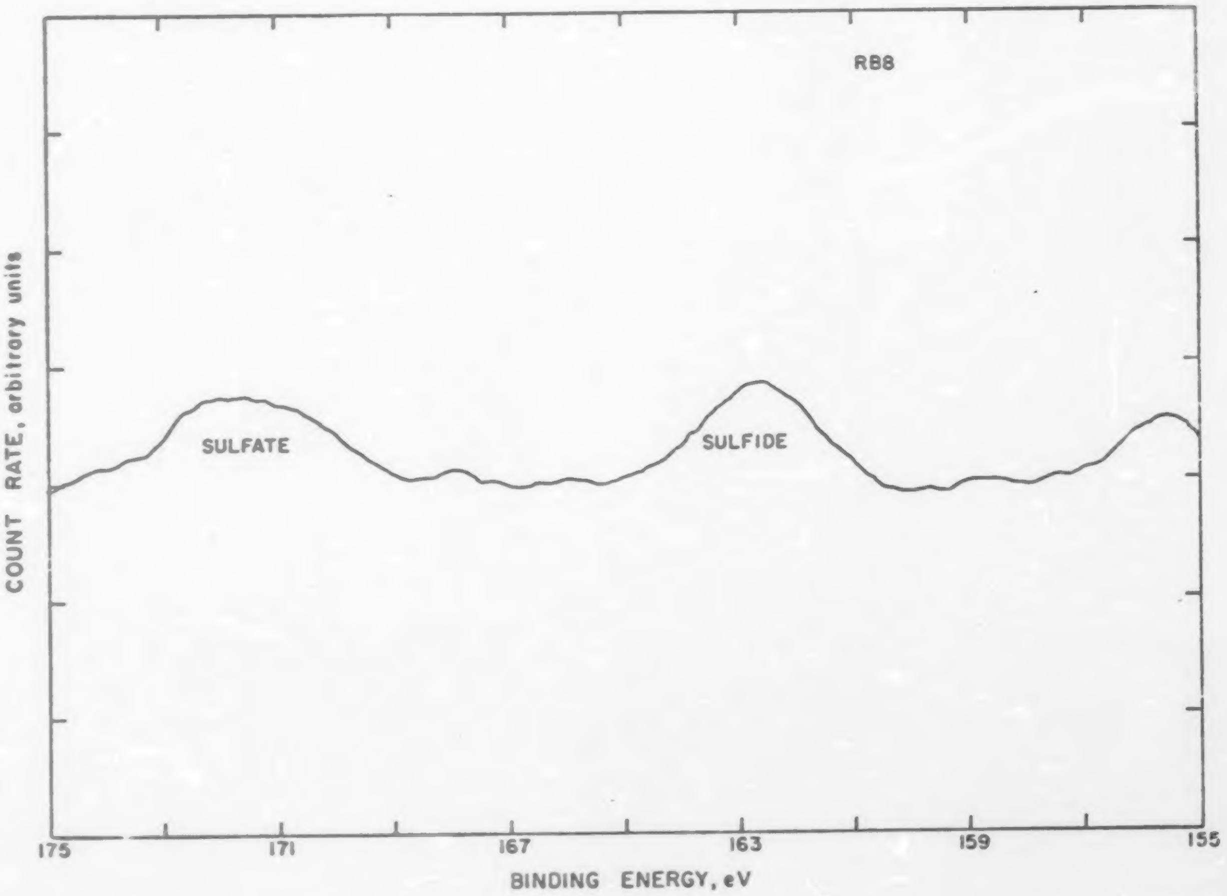

Figure 75. Regenerator bed material from fuel oil gasification, Run No. 4. Sulfur ESCA scan

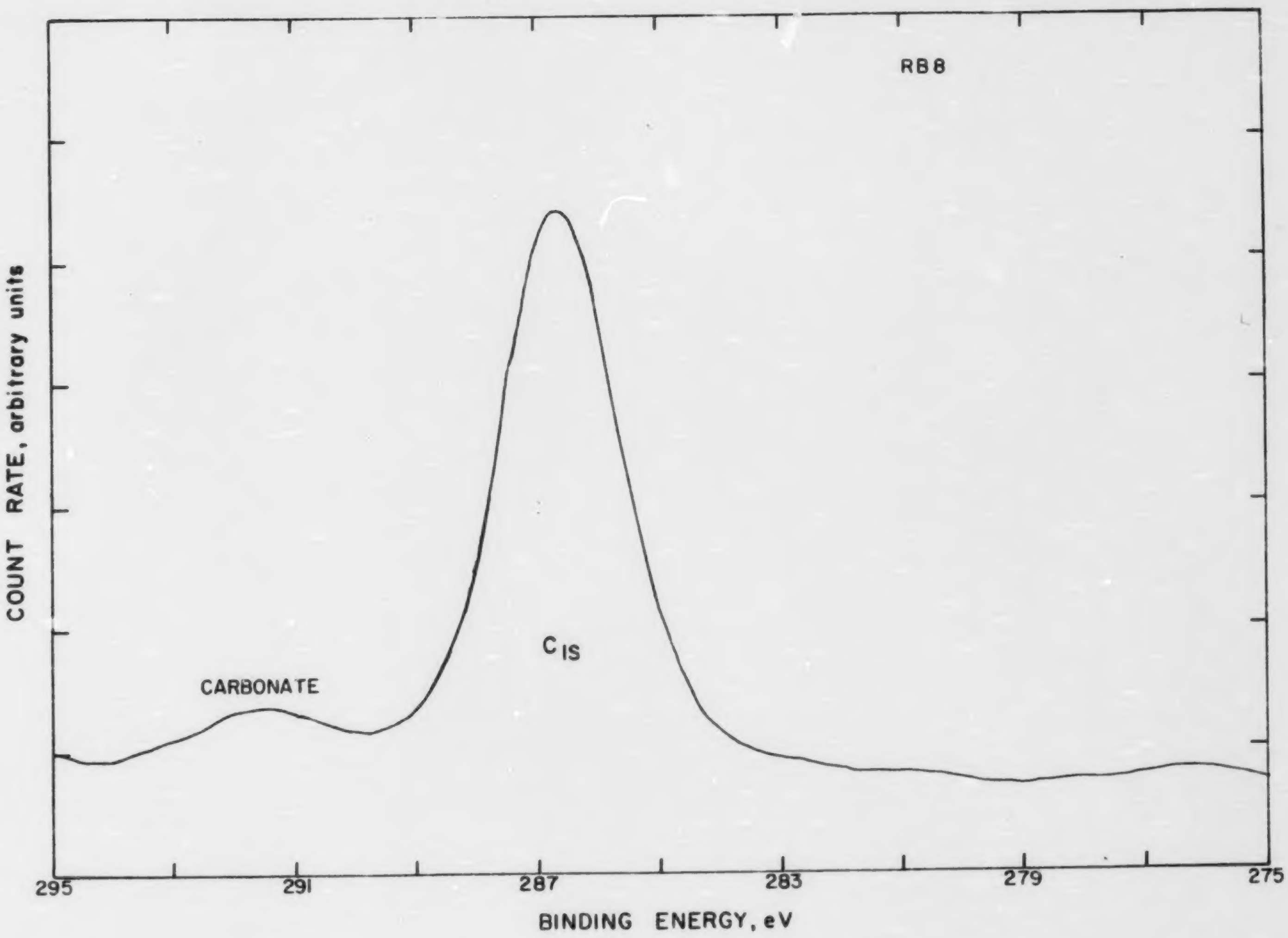

Figure 76. Regenerator bed material from fuel oil gasification, Run No. 4. Carbon ESCA scan

only difference between the two spent stone samples is that surface sulfur here is distributed evenly between sulfate and sulfide. As noted earlier, this distinction is of modest environmental interest.

Table 45. SURFACE CONCENTRATIONS OF SPENT STONE PARTICLES: RUN NO. 4

Element	Abundance, %
O	19.8
C	73.4
Ca	5.2
S	1.6

Leached Stone

The three leached stone samples collected from the outdoor buckets were analyzed by ESCA for surface and subsurface elements. Results of these analyses are presented in Table 46.

Table 46. SURFACE AND SUBSURFACE ELEMENTAL COMPOSITIONS OF LEACHED STONE SAMPLES

	Sample, % abundance					
	SS1		SS3		SS5	
Element	Surface	Sub-surface	Surface	Sub-surface	Surface	Sub-surface
O	52.8	55.8	52.4	59.0	53.8	63.1
Ca	12.0	15.1	12.3	18.3	13.3	20.6
C	33.2	26.2	33.3	21.3	31.0	15.1
S	1.8	1.6	1.9	1.4	1.9	1.3
Si	-	-	-	-	-	1.3

Comparison of these results with the analyses of spent stone in Tables 39 and 45 shows that these samples have a much lower carbon coating and an equivalent surface concentration of sulfur. Because sintered, but unleached stone was not available for analysis, effects of leaching and sintering cannot be separately evaluated.

SUMMARY

Boiler stack gas and stack particulate emissions and solid waste effluents from fuel oil gasification, bitumen gasification and bitumen combustion were sampled and analyzed. The following points summarize the results of environmental interest.

- Stack NO_x emissions are consistently much lower than New Source Performance Standards (NSPS).
- Under normal operating conditions SO_x emissions are lower than NSPS.
- Saturated gasifier stone causes SO_x emissions to exceed NSPS.
- Under normal operating conditions particulate emissions are just barely lower than NSPS.
- During fresh stone feeding particulate emissions exceed NSPS.
- Vanadium is the only trace element whose emission rate presents a potential problem.
- Stack gas and particulate organic emission rates do not present a potential problem.
- Fugitive air emissions from bitumen storage and handling may contain POM.

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SECTION VI

CAFB AIR QUALITY IMPACT ASSESSMENT FOR THE LA PALMA RETROFIT

INTRODUCTION

In a comprehensive environmental assessment the next step after compiling the emissions inventory is to calculate the incremental loadings to the local ambient air, water and soil resulting from the output of all process waste streams. These incremental loadings should then be compared with known human health and ecological effects data in order to assess the environmental acceptability of the process. A complete environmental impact evaluation of this sort is well beyond the scope of this preliminary study.

Rather than being an attempt at a full superficial environmental impact analysis, this Section presents a discussion of meteorological and topographical characteristics of an area which influence the transport of pollutants emitted from a point source. Special emphasis is placed upon the most significant parameters for the La Palma Power Station. This general review of dispersion characteristics in the vicinity of the plant is followed by a detailed diffusion modeling analysis of the expected SO_2 and particulate levels after the installation of the CAFB. Finally, the results of this analysis are compared with Texas emission and ambient air standards.

VARIABLES AFFECTING AMBIENT CONCENTRATIONS

Emission Characteristics

There are a number of point source emission characteristics which affect the subsequent transport for a given pollutant. These include the stack height, stack diameter, gas exit velocity and gas temperature. These parameters, together with the ambient temperature and stability index, are used in the calculation of buoyant plume rise, which is responsible for a greater degree of plume dilution due to an increased effective stack height. A greater source height will also ensure a lesser degree of plume depletion due to dry deposition upon the ground surface. It is sometimes necessary to study the relationship of each source to nearby structures in the area due to their influence in the processes of plume rise retardation or downwash.

Another emission characteristic of interest would be the time variation of the emission rate over a daily, weekly or seasonal period. For example, if a given sector of the population is sensitive to short term episodes of elevated concentrations, then an hourly distribution of emission rates would be of interest, whereas the long term effects of wet and dry deposition of pollutants in the vicinity of a source would require only average annual emission values.

Topographical Characteristics

The general nature of the landscape will exert a significant influence upon the atmospheric transport of pollutants. The channeling of atmospheric pollutants by topographical features such as ridges and valleys is a well known phenomenon. Areas situated near a lake or ocean will in general experience a lower dilution of pollutants due to the resulting higher atmospheric stability when the wind blows across the land from the cooler body of water. Areas having a greater elevation than the base of a stack will usually be exposed to greater pollutant concentrations. Since the area surrounding the La Palma plant is characterized by rather flat terrain, the pollutant transport process is not likely to depend upon topography.

Climatological Characteristics

For the Lower Rio Grande Valley of Texas, the most significant climatological characteristics in terms of transport and diffusion are the prevailing wind direction and the amount of solar insolation. Figure 77 illustrates the frequency distributions of surface wind direction for a number of weather stations in the U.S. The annual "wind rose" for Brownsville, Texas, the closest station to the La Palma facility, shows that for the most part the winds are confined to the east-southeast, southeast and south-southeast directions. The few occasions when northwest winds are present are confined exclusively to the winter months. The strong southeasterly flow off the Gulf of Mexico is driven by high pressure off the southeastern coast and the northeast gulf and is reinforced by a seabreeze which develops during the late morning. The fact that the wind is predominantly from the southeast quadrant will lead to elevated concentrations northwest of the plant for averaging times greater than 1 hour. The solar radiation incident at the surface of the earth is another parameter required for the analysis of concentration levels due to point source emissions. The annual mean daily solar radiation (Langleys) is given in Figure 78 for a number of weather stations throughout the country. The value of 442 Langleys reported for Brownsville would argue for a higher frequency of unstable atmospheric conditions than for stations in the northeastern part of the country. As indicated later in this Section (Figures 84 through 89), these unstable conditions will lead to higher concentrations for receptors located near the plant and reduced levels at greater distances from the source.

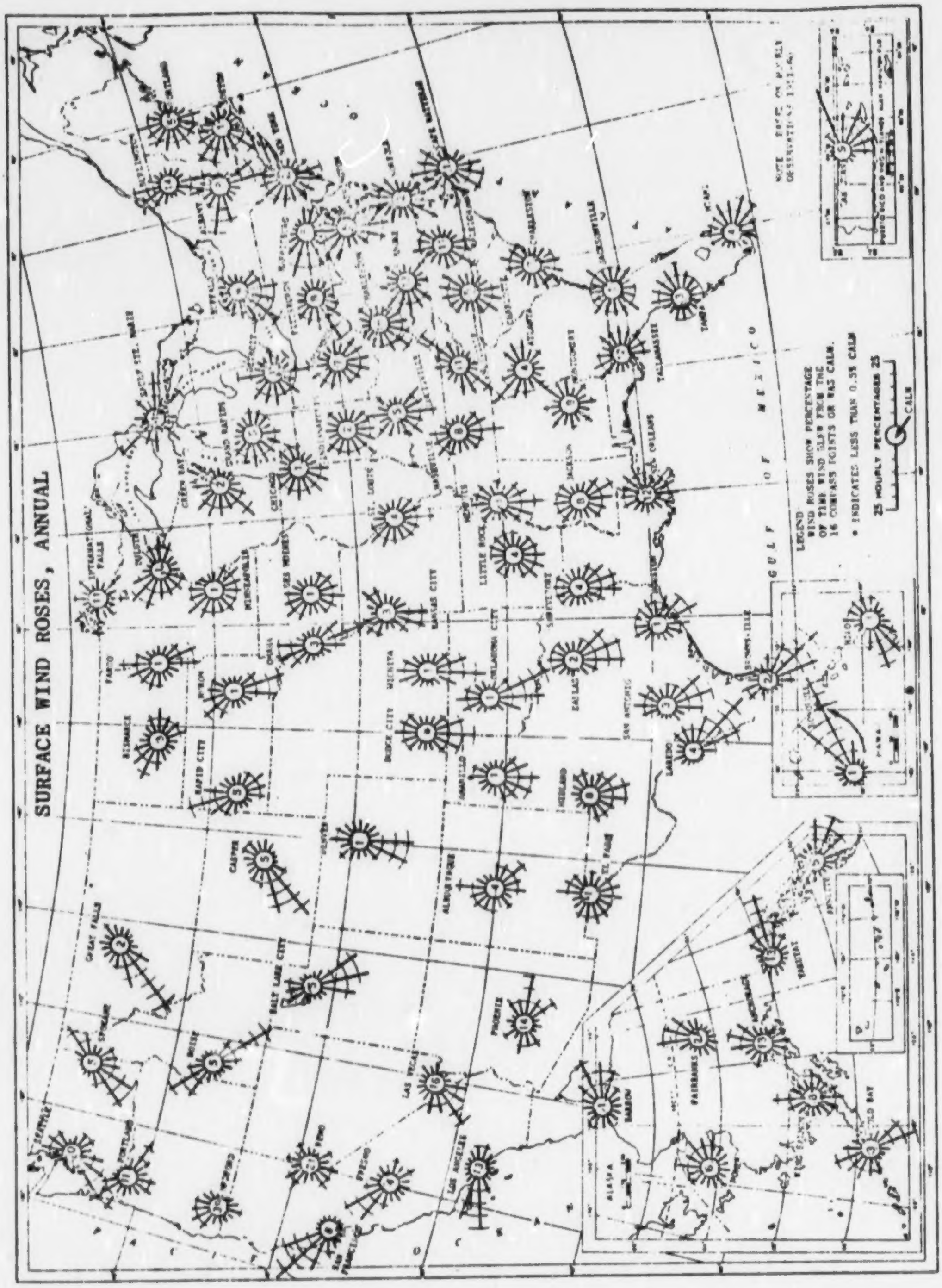
SURFACE WIND ROSES, ANNUAL
LEGEND
WIND ROSES SHOW PERCENTAGE OF TIME WIND BLEW FROM THE 16 COMPASS POINTS OR WAS CALM.
• INDICATES LESS THAN 0.5% CALM
25 HOURLY PERCENTAGES 25
CALM
GULF OF MEXICO
SEATTLE
PORTLAND
SPOKANE
GREAT FALLS
BOISE
SALT LAKE CITY
RENO
FRESNO
SAN FRANCISCO
LOS ANGELES
LAS VEGAS
PHOENIX
CASPER
DENVER
ALBUQUERQUE
EL PASO
RAPID CITY
BISMARCK
FARGO
OMAHA
DODGE CITY
AMARILLO
MIDLAND
SAN ANTONIO
LAREDO
BROWNSVILLE
HOUSTON
DALLAS
OKLAHOMA CITY
WICHITA
KANSAS CITY
DES MOINES
MINNEAPOLIS
DULUTH
INTERNATIONAL FALLS
GREEN BAY
CHICAGO
GRAND RAPIDS
SAULT STE. MARIE
ST. LOUIS
MEMPHIS
LITTLE ROCK
SHREVEPORT
JACKSON
NEW ORLEANS
MONTGOMERY
ATLANTA
TALLAHASSEE
TAMPA
MIAMI
JACKSONVILLE
CHARLESTON
NASHVILLE
INDIANAPOLIS
BUFFALO
PITTSBURGH
CAPE HATTERAS
ALASKA
BARROW
FAIRBANKS
COLD BAY

Figure 77. Annual surface wind roses[1]

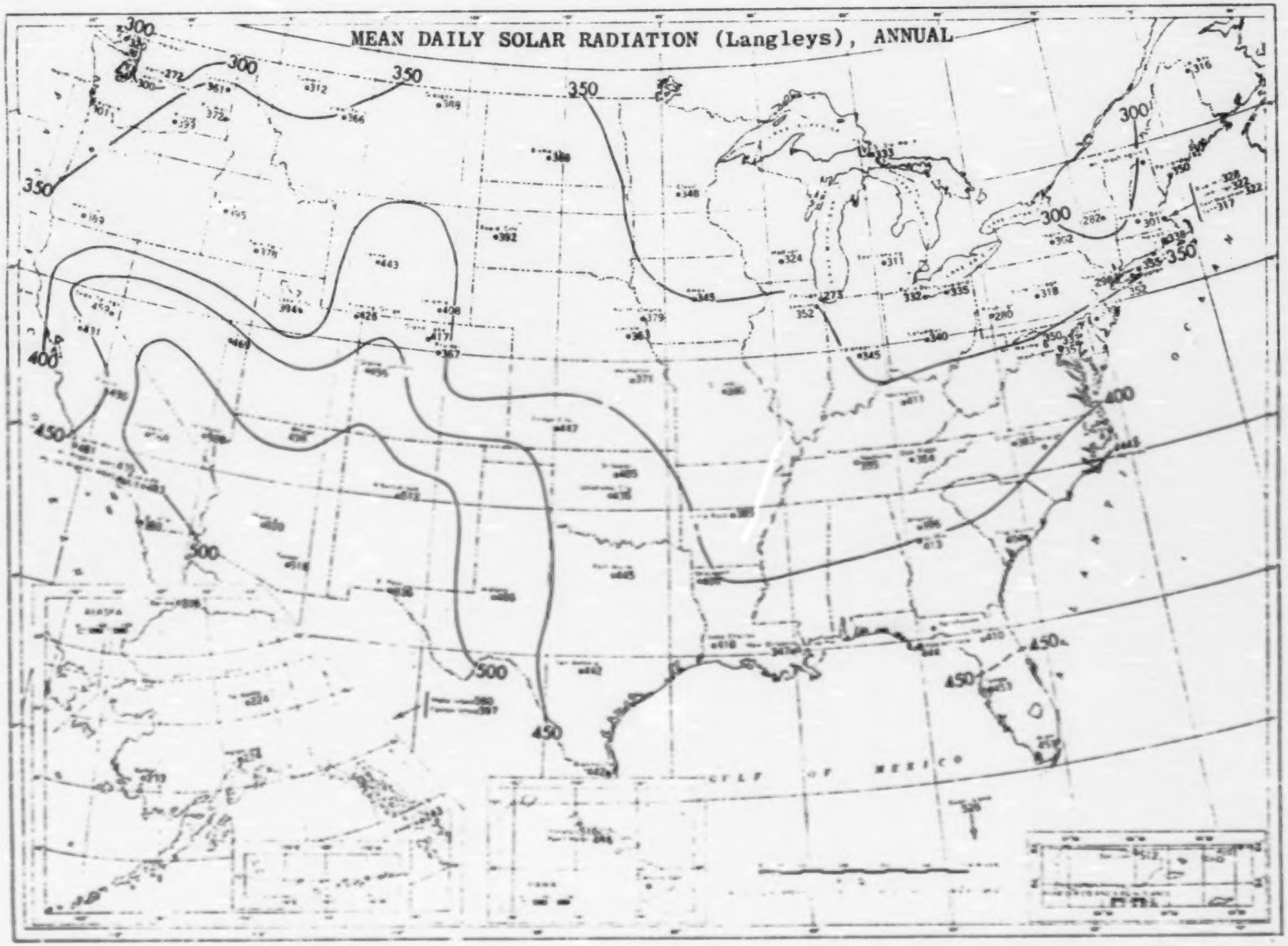
MEAN DAILY SOLAR RADIATION (Langleys), ANNUAL
300
350
400
450
500
GULF OF MEXICO

Figure 78. Annual mean daily solar radiation[1]

As indicated by the modeling analysis (see below), the predicted concentrations will be quite sensitive to windspeed because this parameter is used in the determination of plume rise, stability class and the amount of plume dilution. On an annual basis, however, the surface windspeed will average about 5.4 m/s (12 miles per hour) (see Figure 79) which is only slightly greater than the average for the entire country.

The remaining two climatological variables which will affect pollutant dispersion in the vicinity of the La Palma site are the mixing depth and the ambient temperature. The mixing depth may be roughly defined as the atmospheric boundary layer near the earth's surface in which the turbulent diffusion mechanisms predominate. In response to daytime heating of the land surface, the depth of this layer may exceed 1 or 2 kilometers, but will be considerably reduced during nighttime hours. The top of this layer, marked by a discontinuity in the temperature profile, acts as a barrier to the vertical migration of material released within the layer. The mixing height data presented in Figures 80 and 81 indicate that the La Palma site is characterized by lower afternoon mixing depths and greater morning mixing depths than the country as a whole. The actual manner in which these mixing depths enter into the dispersion calculations is explained in the modeling analysis section. The relatively high ambient temperature for the La Palma site (annual average, 23°C (74°F)) will result in a slightly reduced plume rise as compared with areas in the northern half of the U.S., but this effect would mean only a few percent change in the annual concentration.

DISPERSION MODELING ANALYSIS

Description of Modeling Techniques

This section addresses the quantitative evaluation of short-term SO_2 and suspended particulate (TSP) levels in the vicinity of the La Palma facility for the CAFB configuration. In the case of SO_2, worst 1-hour

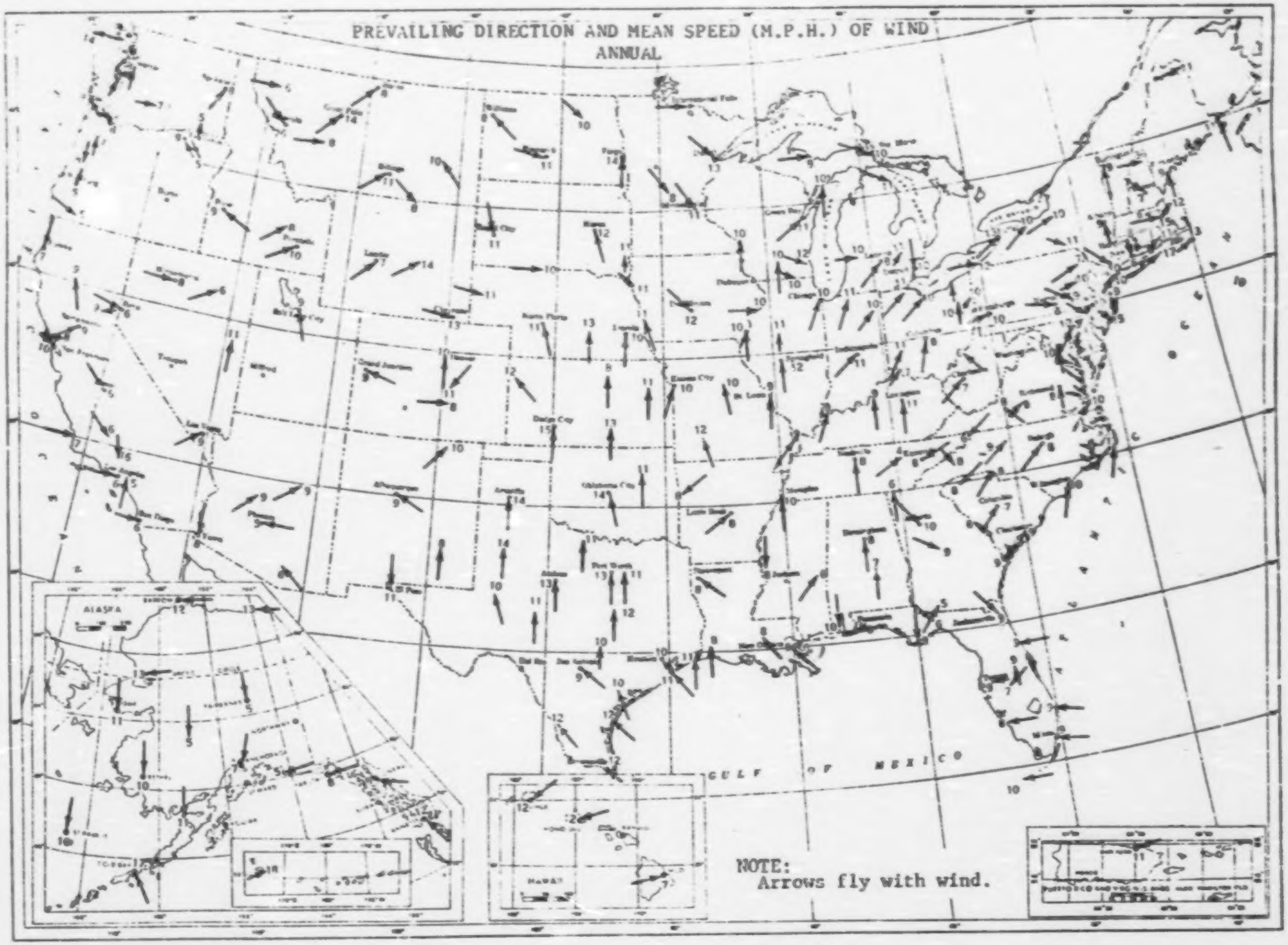
PREVAILING DIRECTION AND MEAN SPEED (M.P.H.) OF WIND
ANNUAL
ALASKA
HAWAII
GULF OF MEXICO
NOTE:
Arrows fly with wind.

Figure 79. Annual mean windspeeds and resultant wind directions[1]

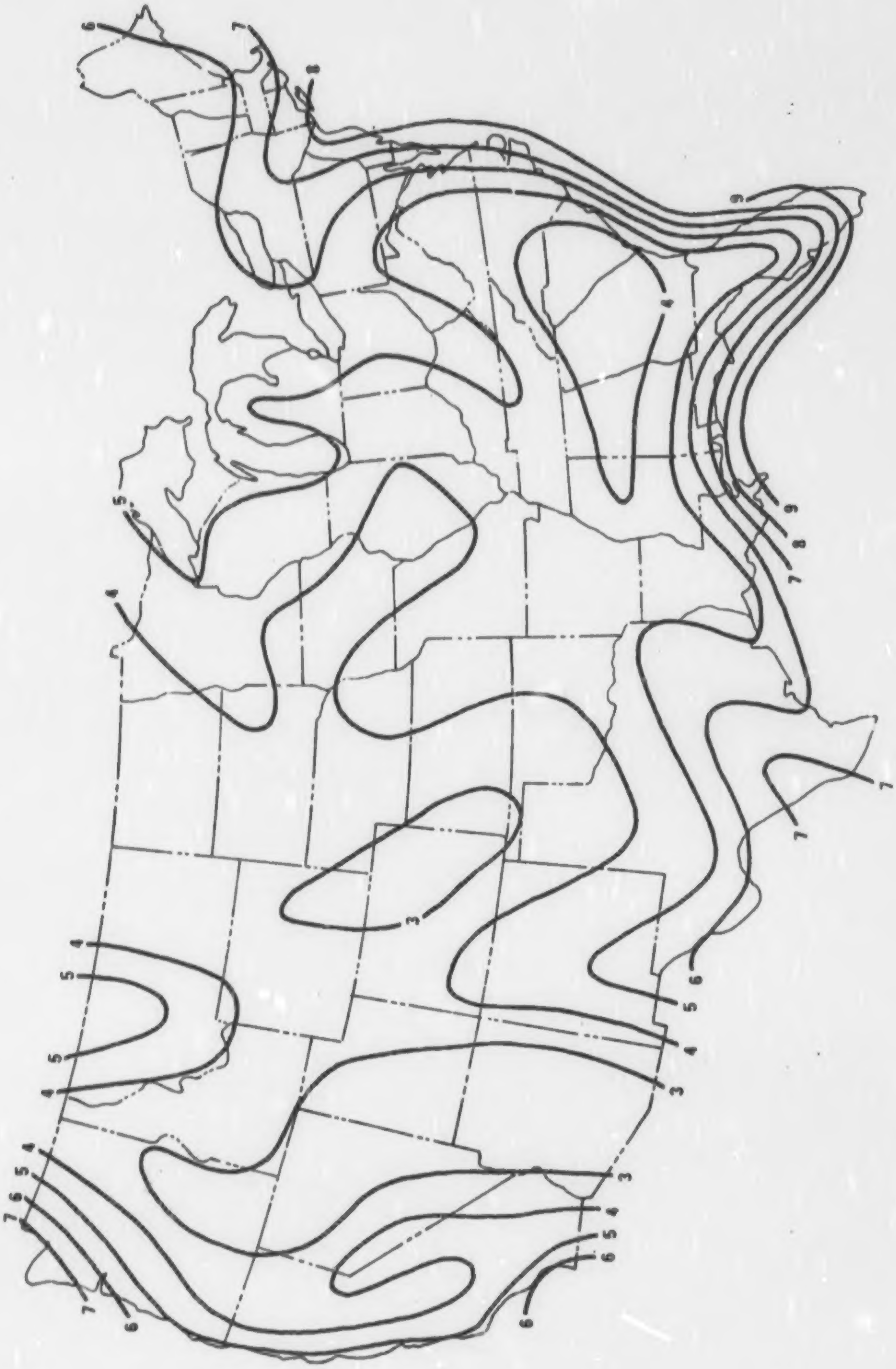

Figure 80. Isopleths (m x 10^2) of mean annual morning mixing heights[2]

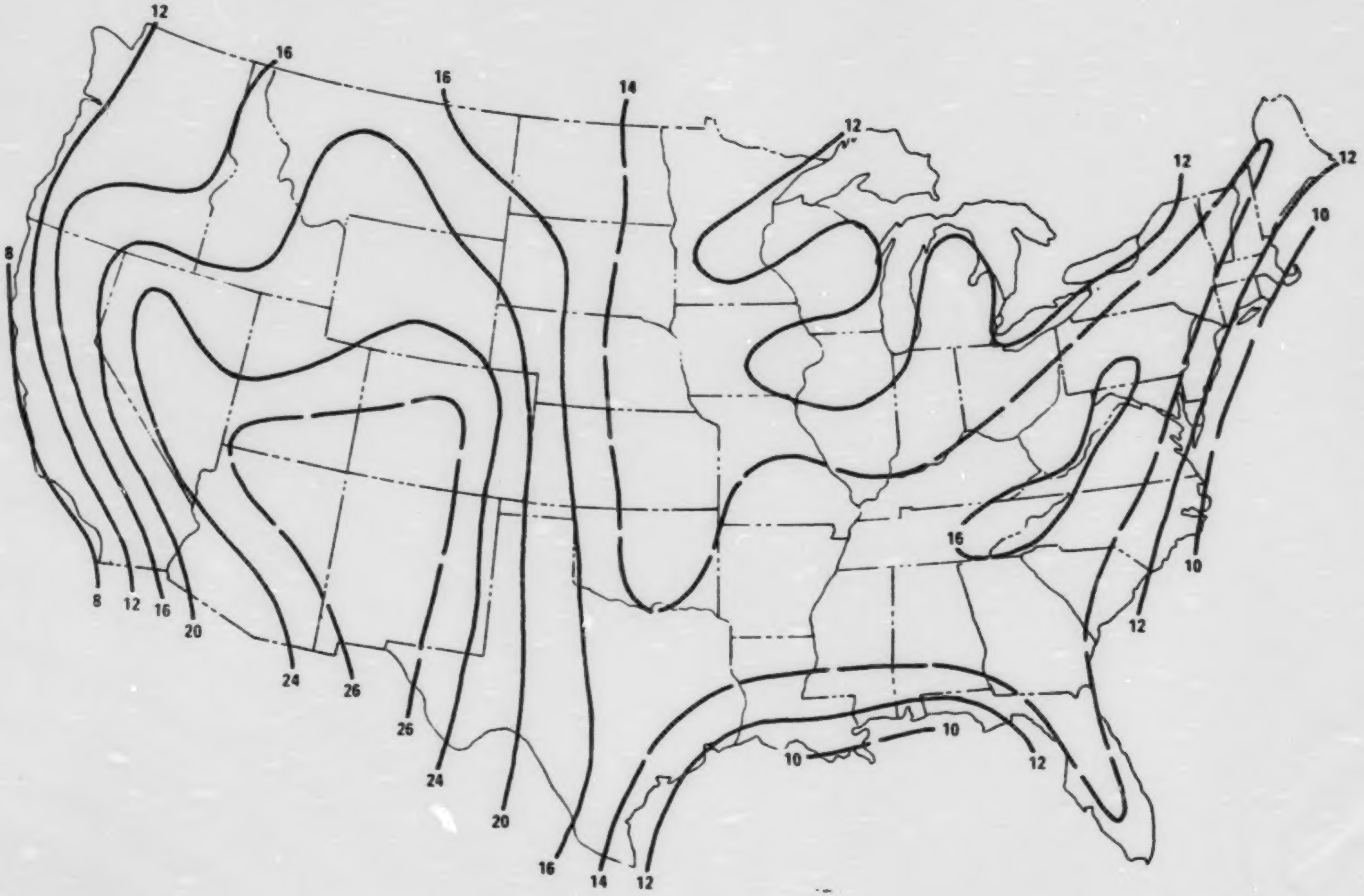
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Figure 81. Isopleths (m x 10^2) of mean annual afternoon mixing heights[2]

predicted concentrations can be extrapolated to highest 3-hour and 24-hour averages through the application of peak to mean ratio statistics derived from an analysis of air quality data collected in the vicinity of isolated point sources. Highest 24-hour averages for TSP can be determined in the same manner. The expression used for evaluation of 1-hour pollutant concentrations downwind of a point source is the Gaussian plume equation[3,4] given by

$$\chi(x,y,z) = \frac{Q \exp\left(\frac{-y^2}{2\sigma_y{}^2(x)}\right)}{2\pi\ \sigma_y(x)\ \sigma_z(x)\ u} \left[\exp\left(-\frac{\left(z-h(x)\right)^2}{2\sigma_z{}^2\ (x)}\right) + \exp\left(-\frac{\left(z+h(x)\right)^2}{2\sigma_z{}^2\ (x)}\right) \right] \quad (1)$$

where x = distance along plume axis (m)

y = horizontal distance from plume axis (m)

z = distance above surface (m)

$\chi(x,y,z)$ = concentration of pollutant (g/m^3)

Q = effective emission rate of pollutant distance x (g/sec)

$\sigma_y(x)$, $\sigma_z(x)$ = horizontal and vertical dispersion coefficients for a particular atmospheric stability (A,B,C,D,E,F)

u = windspeed at source height (m/sec)

$h(x)$ = effective emission height at distance x (m).

The variation of σ_y and σ_z with x for each of the six stability classifications (A to F) has been determined from a number of experiments[3] based upon low level releases of tracer material and do not strictly apply to elevated sources or for downwind distances greater than about 5 km. The usual procedure, however, is to assume that these results are approximately true for greater source heights and that they may be extrapolated to longer distances. The choice of a given stability will depend upon windspeed, cloud cover and sun elevation. The basis for the selection is given in Table 47. The variation of σ_y and σ_z with distance is shown in Figures 82 and 83. The second exponential term in brackets on the right side of Equation (1) is an "image" point source contribution which is required to meet the zero flux boundary condition at the ground surface ($z = 0$). The effective source strength $Q_1(x)$ will be different than the strength $Q_1(0)$ at the point of emission due to wet deposition, dry fallout, and chemical transformation. The effective stack height $h(x)$ will be greater than the actual stack height h_o due to the buoyancy of the plume.[5] The expression for $h(x)$ for stabilities A through D is given by

$$h(x) = h_o + \Delta h \qquad (2)$$

where $\Delta h = 1.6F^{1/3}\, u^{-1}\, x^{2/3}$ for $x \leq 3.5x^*$

$\Delta h = 1.6F^{1/3}\, u^{-1}\, (3.5x^*)^{2/3}$ for $x > 3.5x^*$

$x^* = 14F^{5/8}$ when $F < 55\ m^4/sec^3$

$x^* = 34F^{2/5}$ when $F \geq 55\ m^4/sec^3$

$$F = gwr^2 \left(\frac{T_s - T_e}{T_s}\right)$$

g = gravitational acceleration (m/sec^2)

w = stack gas ejection velocity (m/sec)

r = radius of stack (m)

T_s = stack gas temperature (^oK)

T_e = air temperature (^oK).

Table 47. RELATION OF PASQUILL STABILITY CLASSES TO WEATHER CONDITIONS

Surface wind speed (at 10 m), m sec^{-1}	Day			Night	
	Incoming solar radiation			Thinly overcast or $\geq$ 4/8 low cloud	$\leq$ 3/8 cloud
	Strong	Moderate	Slight		
< 2	A	A-B	B		
2-3	A-B	B	C	E	F
3-5	B	B-C	C	D	E
5-6	C	C-D	D	D	D
> 6	C	D	C	D	D

The neutral class, D, should be assumed for overcast conditions during day or night.

A - Extremely unstable
B - Moderately unstable
C - Slightly unstable
D - Neutral
E - Slightly stable
F - Moderately stable

Pasquill stability classes	σ_A
A, extremely unstable	25.0°
B, moderately unstable	20.0°
C, slightly unstable	15.0°
D, neutral	10.0°
E, slightly stable	5.0°
F, moderately stable	2.5°

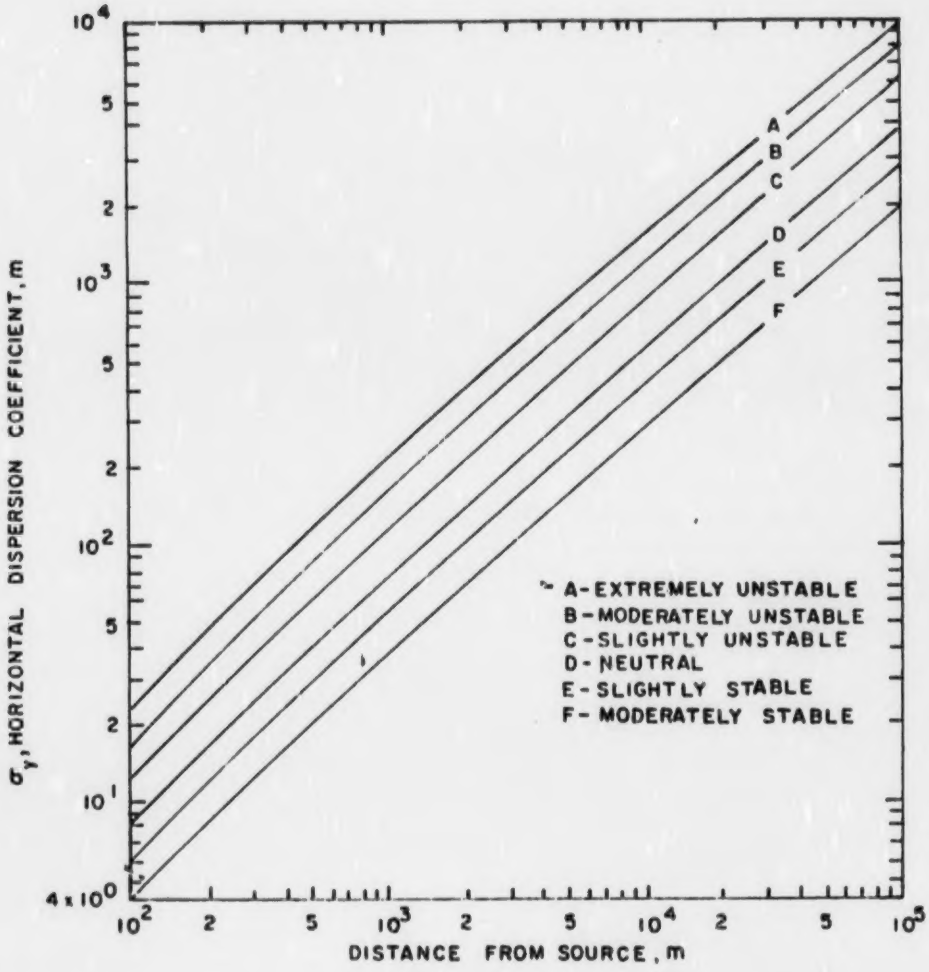

Figure 82. Horizontal dispersion coefficient as a function of distance for Pasquill's stability types[3]

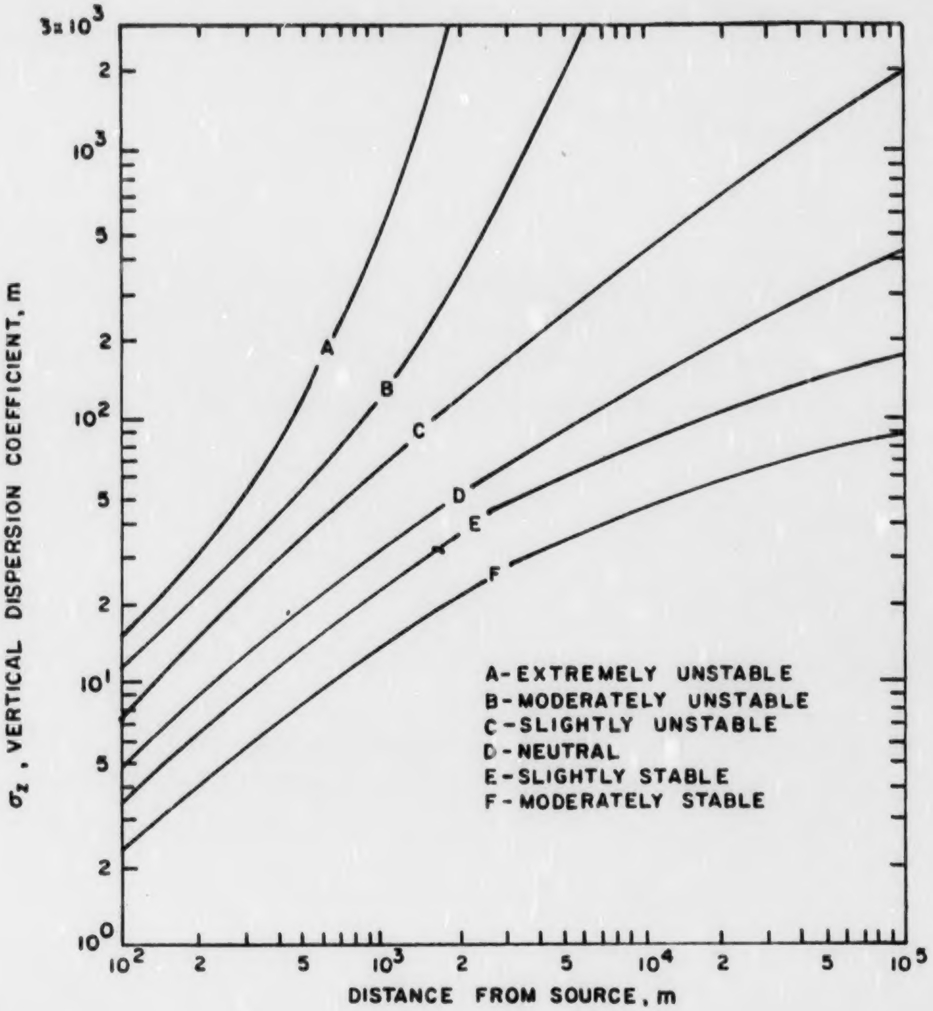

Figure 83. Vertical dispersion coefficient as a function of distance for Pasquill's stability types[3]

For stability classes E and F the plume rise becomes

$$\Delta h = 2.9 \left(\frac{F}{us}\right)^{1/3} \tag{3}$$

where $s = \frac{g}{T_e} \frac{d\theta}{dz}$

$\frac{d\theta}{dz} = 0.02\ ^{o}K/m$ for stability E

$\frac{d\theta}{dz} = 0.035\ ^{o}K/m$ for stability F

The windspeed (u) at source height (h_o) may be related to the windspeed (u_m) measured at a standard distance (h_m) above ground level according to the following power law:[7]

$$u = u_m \left(\frac{h}{h_m}\right)^{p} \tag{4}$$

where the exponent p depends upon the stability class.

The presence of the mixing boundary may be accounted for by the incorporation of multiple image sources as was done to satisfy the zero flux condition at ground level. Equation (1) may then be generalized to give[7]

$$\chi(x,y,z) = \frac{Q \exp\left(\frac{-y^2}{2\,\sigma_y^{\,2}(x)}\right)}{2\pi\,\sigma_y(x)\,\sigma_z(x)} \Bigg\{ \exp\left(-\frac{\left(z - h(x)\right)^2}{2\,\sigma_z^{\,2}(x)}\right)$$

$$+ \exp\left(-\frac{\left(z + h(x)\right)^2}{2\,\sigma_z^{\,2}(x)}\right) + \sum_{j=1}^{n} \exp\left(-\frac{(z - h(x) - 2jL)^2}{2\,\sigma_z^{\,2}(x)}\right)$$

$$+ \exp\left(-\frac{(z + h(x) - 2jL)^2}{2\,\sigma_z^{\,2}(x)}\right) + \exp\left(-\frac{(z - h(x) + 2jL)^2}{2\,\sigma_z^{\,2}(x)}\right)$$

$$+ \exp\left(-\frac{(z + h(x) + 2jL)^2}{2\,\sigma_z^{\,2}(x)}\right)\Bigg]\Bigg\} \qquad (5)$$

where L = depth of the mixing layer (m)

n = number of images considered

In practice, only the first few image terms contribute significantly to the overall ambient concentration. For distances greater than 2 x_L, where x_L is given by $\sigma_z\ (x_L) = 1.6L$, Equation (5) may be approximated by

$$\chi_1(x,y,z) = \frac{Q \exp\left(\frac{-y^2}{2\,\sigma_y^{\,2}(x)}\right)}{\sqrt{2\pi}\,\sigma_y(x)\ u\ L} \qquad x > 2\,x_L \qquad (6)$$

This discussion of diffusion modeling techniques has so far neglected the aerodynamic effects caused by buildings adjacent to the stack. Low exit velocities and the presence of nearby buildings may result in a reduction of plume rise due to the low pressure in the wake of the stack or building. In certain cases the plume may actually be brought to the ground a short distance downwind of the stack. Effective stack height corrections due to these effects have been estimated by Briggs.[8] The first correction in stack height is due to the stack aerodynamic effect.

$$h' = h + 2\ (w/u - 1.5)D \tag{7}$$

where h = actual stack height (m)

w = stack gas exit velocity (m/sec)

u = windspeed (m/sec)

D = stack diameter (m)

$\frac{\omega}{u} \leq 1.5$

The next stack height correction will depend upon building height (h_b) and is given by one of the following three expressions:

Case 1.

$$h'' = h' \quad \text{if } h > 2.5\ h_b \tag{8}$$

Case 2.

$$h'' = 0 \quad \text{if } h' \leq 1.5\ h_b \tag{9}$$

Case 3.

$$h'' = 2h' - 2.5\ h_b \quad \text{if } 1.5\ h_b < h' \leq 2.5\ h_b \tag{10}$$

The standard plume rise correction due to buoyancy effects is then applied to cases 1 and 3. For case 2 no buoyancy term is added, but an initial dilution volume of cross-sectional area h_b^2 is assumed.

Model Calculations

The following model input parameters will be used for air quality predictions at the La Palma plant:

Q (source strength): SO_2, TSP = 17 g/sec, 2.0 g/sec
r (stack radius at outlet) = 1.14 m
w (stack gas exit velocity) = 6.55 m/sec
T_s (stack gas temperature) = 455°K
T_e (ambient temperature) = 297°K
h (stack height) = 38.7 m
h_b (building height) = 15.5 m
L (mixing height) = 1300 m.

Figures 84 through 89 display hourly plume centerline SO_2 concentrations calculated by use of Equation (1) and the input parameters listed above. Concentration predictions are developed for a wide range of atmospheric stabilities and windspeeds. The results indicate that maximum 1-hour concentrations would be approximately 100 $\mu g/m^3$ and that maximum 1-hour particulate levels would be a factor of 8 lower. Because concentrations for longer average times will be lower than the 1-hour values, these results indicate that both the federal and state ambient air quality standards will be met (see Tables 48 and 49).

These input data can also be used to determine whether plume rise retardation or downwash is likely to be significant at La Palma. According to Equation (7), the greatest stack height reduction due to plume rise retardation will be 6.8 m. Therefore, complete downwash is not possible according to the restriction given by Equation (9). Partial downwash is possible, however, according to Equation (10). Evaluating Equations (7)

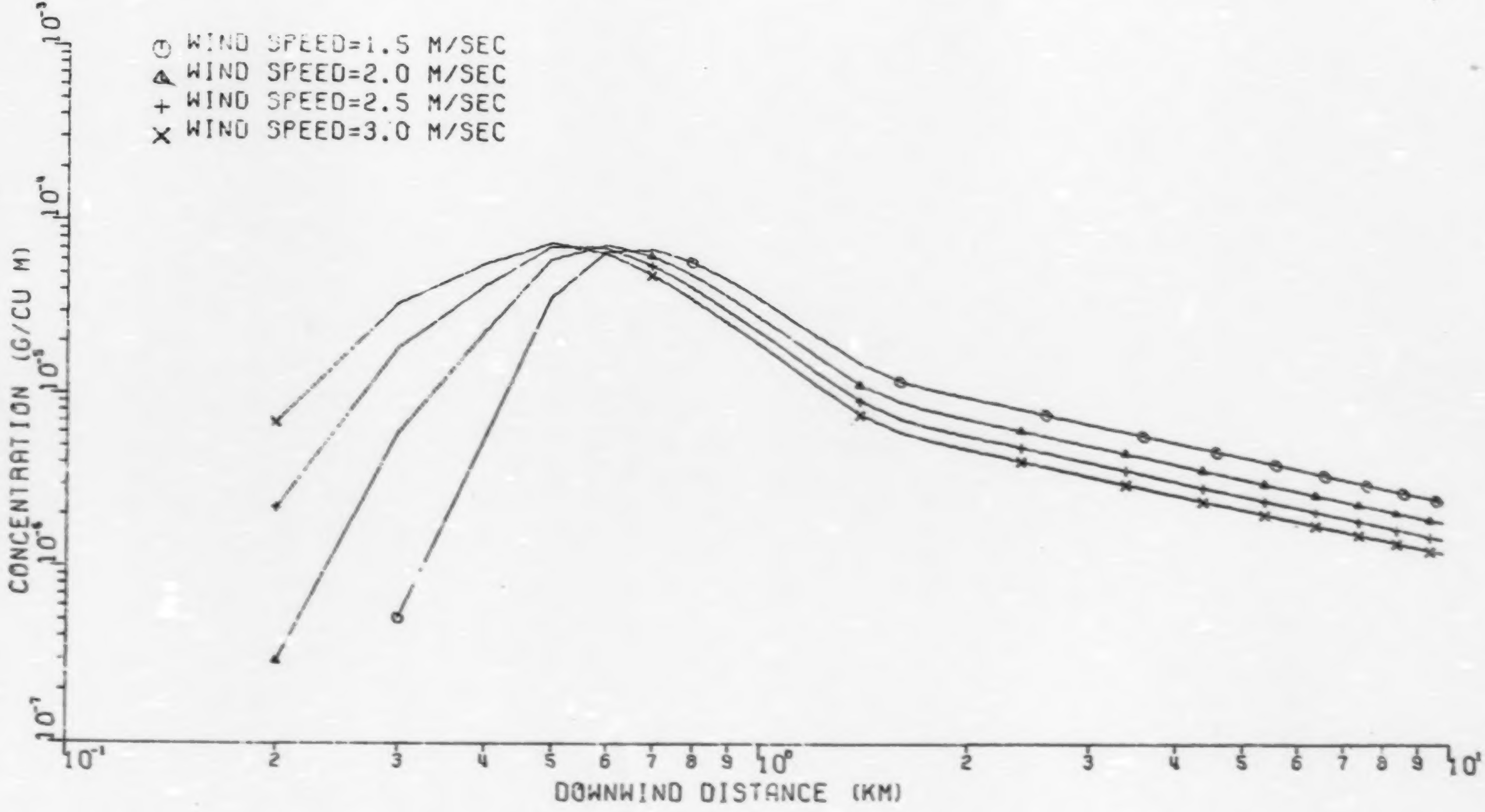

Figure 84. SO_2 concentrations versus downwind distance for stability class 1

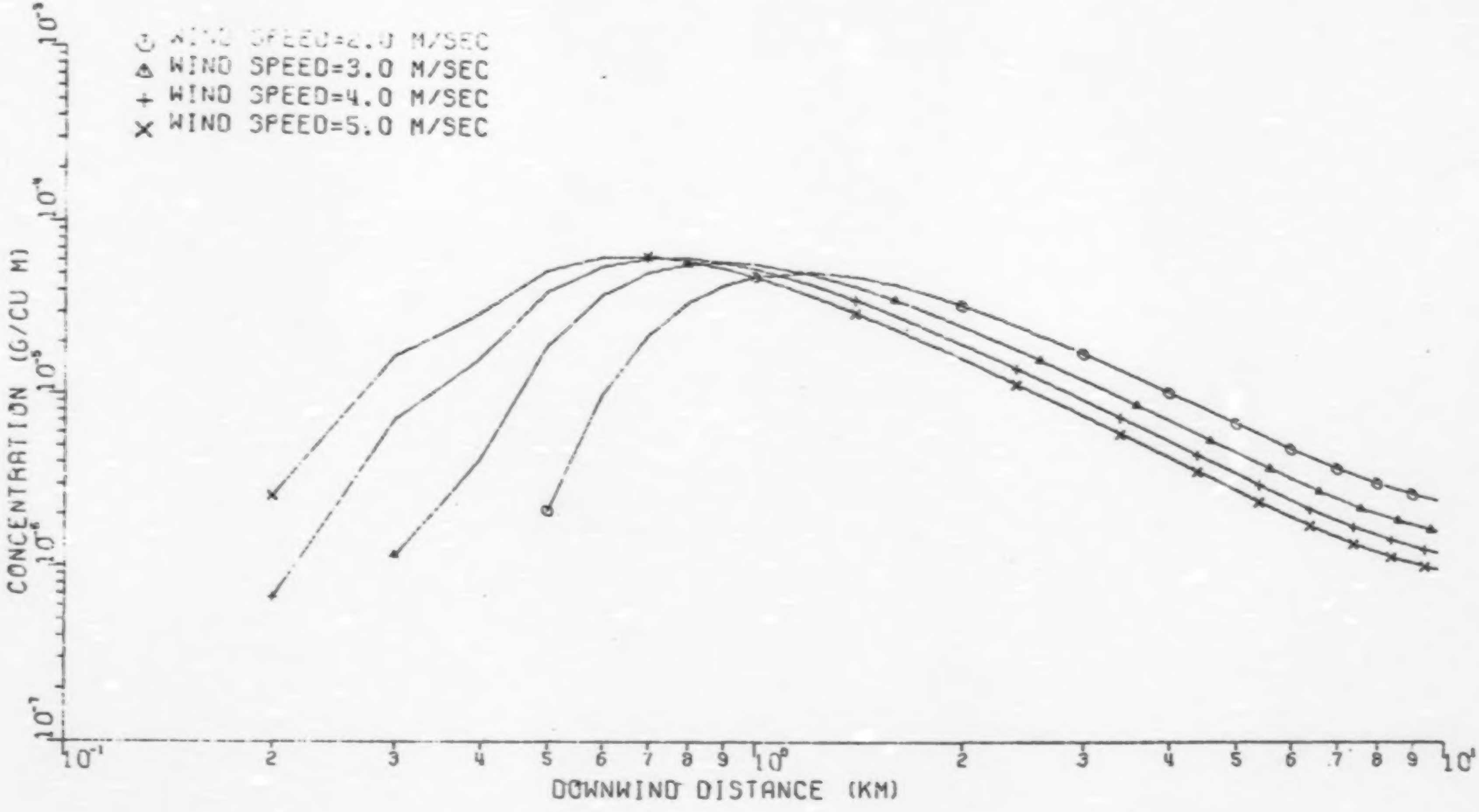

Figure 85. SO_2 concentration versus downwind distance for stability class 2

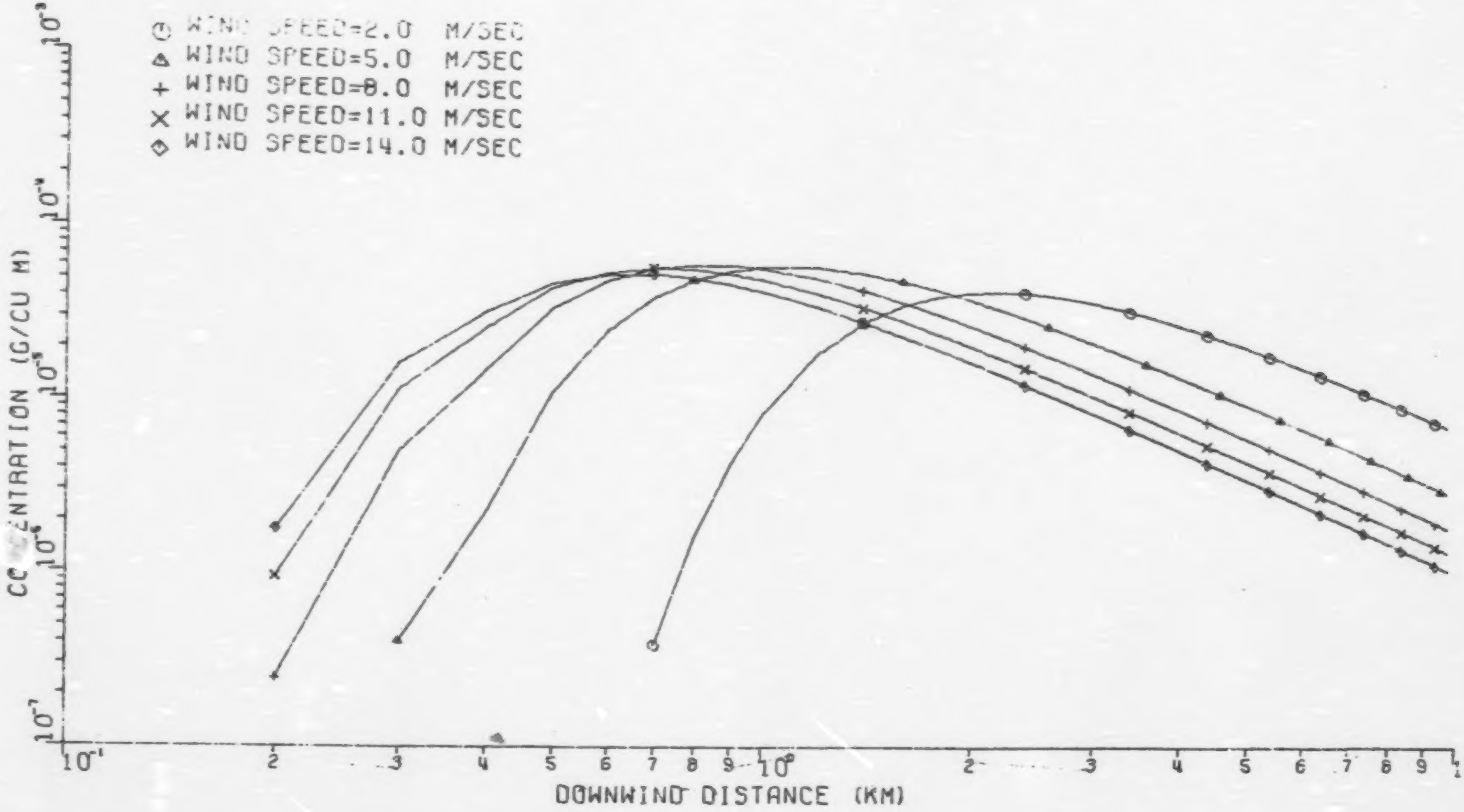

Figure 86. SO_2 concentration versus downwind distance for stability class 3

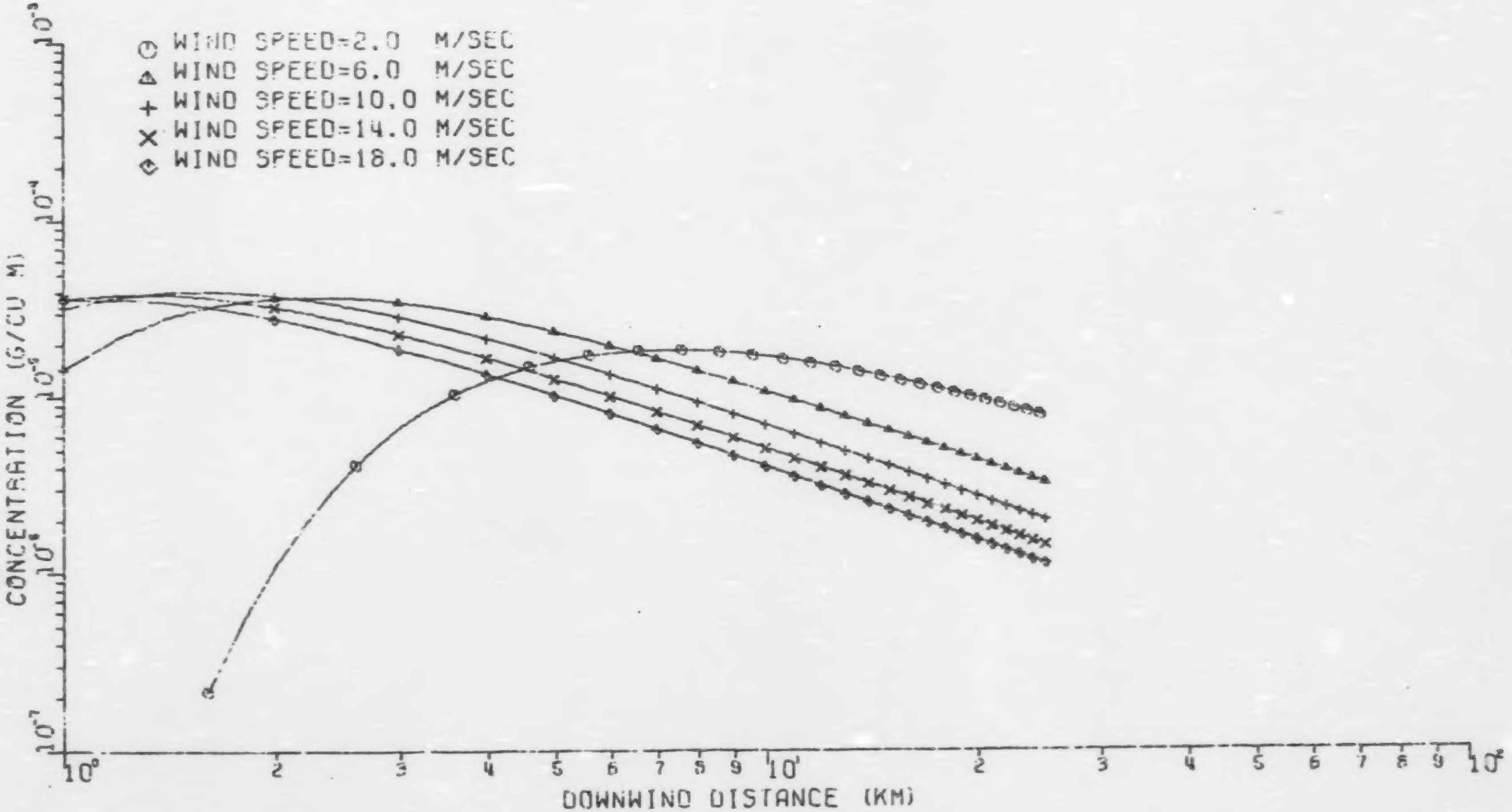

Figure 87. SO_2 concentration versus downwind distance for stability class 4

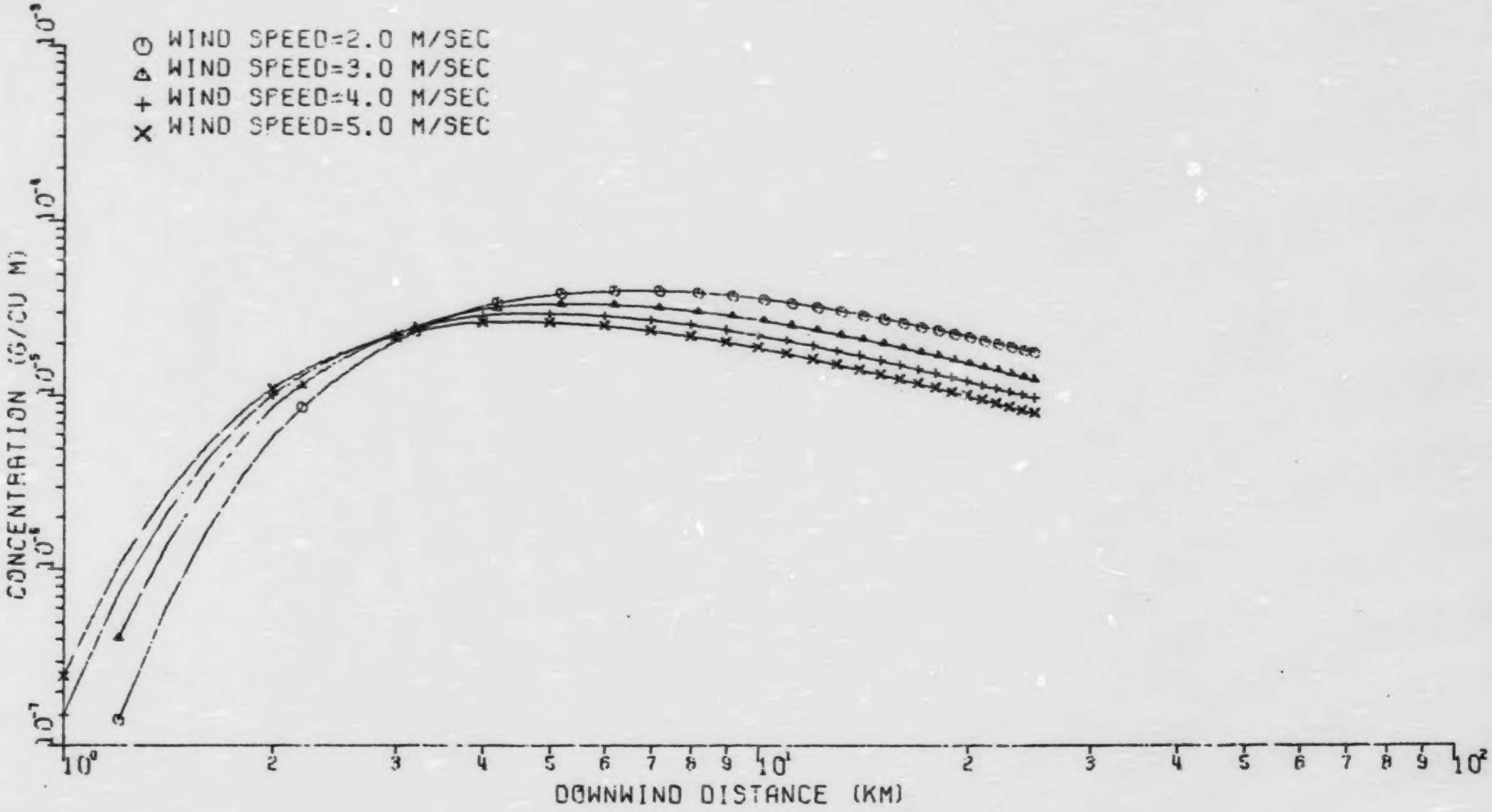

Figure 88. SO_2 concentration versus downwind distance for stability class 5

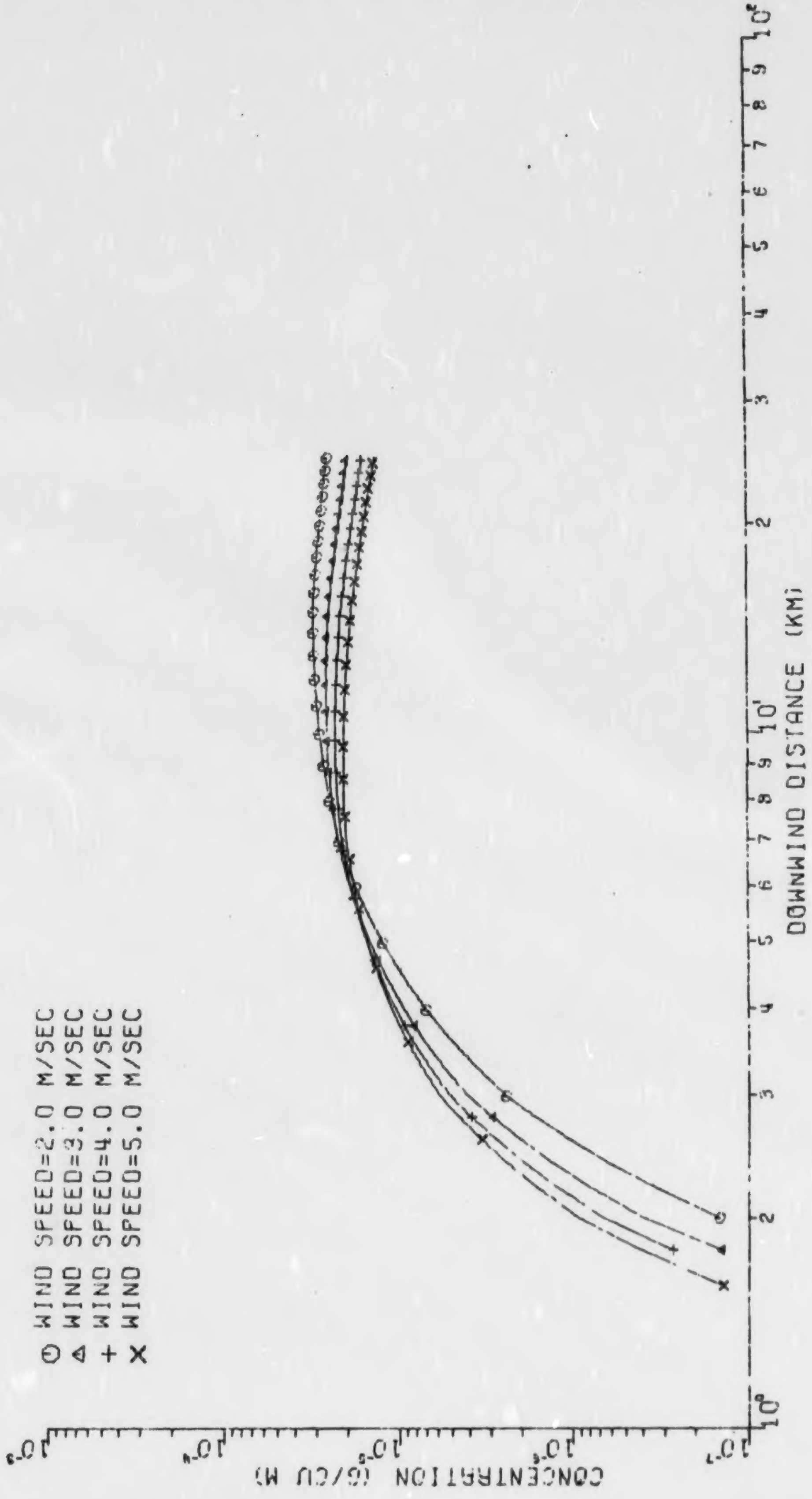

Figure 89. SO_2 concentration versus downwind distance for stability class 6

Table 48. NATIONAL AMBIENT AIR QUALITY STANDARDS

Pollutant	Measurement classification	Primary standards			Secondary standards		
		μg/m^{3} [a]	ppm[b]	mg/m^{3} [c]	μg/m^{3} [a]	ppm[b]	mg/m^{3} [c]
Suspended particulates	Annual geometric mean	75	-	-	60	-	-
	maximum 24-hour average, 1/yr	260	-	-	150	-	-
Sulfur oxides measured as SO_2	Annual arithmetic mean	80	0.03	-	-	0.02	-
	maximum 24-hour average, 1/yr	365	0.14	-	260	0.10	-
	maximum 3-hour average, 1/yr	-	-	-	1300	0.50	-
Carbon monoxide, CO	Maximum 8-hour average, 1/yr	-	9	10	-	9	10
	maximum 1-hour average, 1/yr	-	35	40	-	35	40
Photochemical oxidants	Maximum 1-hour average, 1/yr	160	0.08	-	160	0.08	-
Hydrocarbons	Maximum 3-hour average, 6-9 am, 1/yr	160	0.24	-	160	0.24	-
Nitrogen dioxide, NO_2	Annual arithmetic mean	100	0.05	-	100	0.05	-

[a] Micrograms per cubic meter.

[b] Parts per million (T = 25°C, P = 760 mmHg).

[c] Milligrams per cubic meter.

and (10) using the model input data, the following expression for the source height which incorporates both plume rise retardation and downwash results:

$$h'' = 24.97 + \frac{59.74}{u} \quad \text{for } u \geq 4.37 \text{ m/sec}$$

$$h'' = 38.65 \quad \text{for } u < 4.37 \text{ m/sec.}$$

Table 49. TEXAS AMBIENT PARTICULATE STANDARDS

Concentration averaging time	Maximum concentrations, $\mu g/m^3$
5 hours	100
3 hours	200
1 hour	400

After incorporating the above plume rise retardation effects, and repeating the calculation of plume centerline concentrations for stabilities 1 and 2, it was found that the maximum 1-hour concentrations are not significantly increased (see Figures 90 and 91).

Texas emission standards[9] for particulates are given in terms of the effluent flow rate according to Table 50. The flow rate at the La Palma facility is approximately 57,000 acfm with an associated particulate emission rate of 15 lb/hr, a configuration which falls well within the limits set forth in Table 50. Since the unit at La Palma will only have a heat input of 210 million Btu per hour, it does not fall under the following regulation for oil- or gas-fired steam generators:

> 105.32 No person may cause, suffer, allow or permit emissions of particulate matter from any oil or gas fuel fired steam generator with a heat input greater than 2500 million Btu per hour to exceed 0.1 lb. per million Btu heat input maximum 2-hour average.

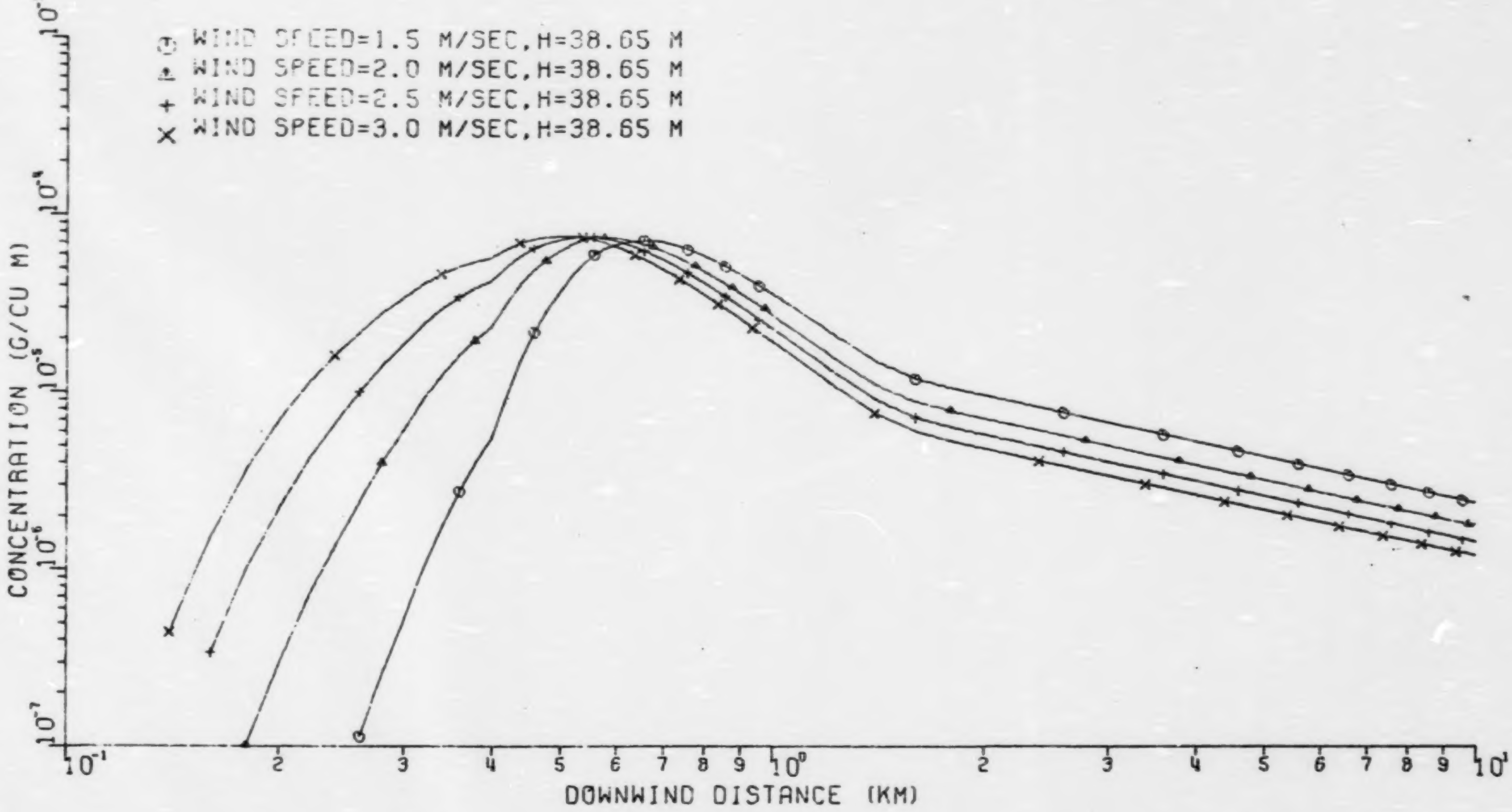

Figure 90. SO_2 concentration versus downwind distance for stability class 1 (plume rise retardation included)

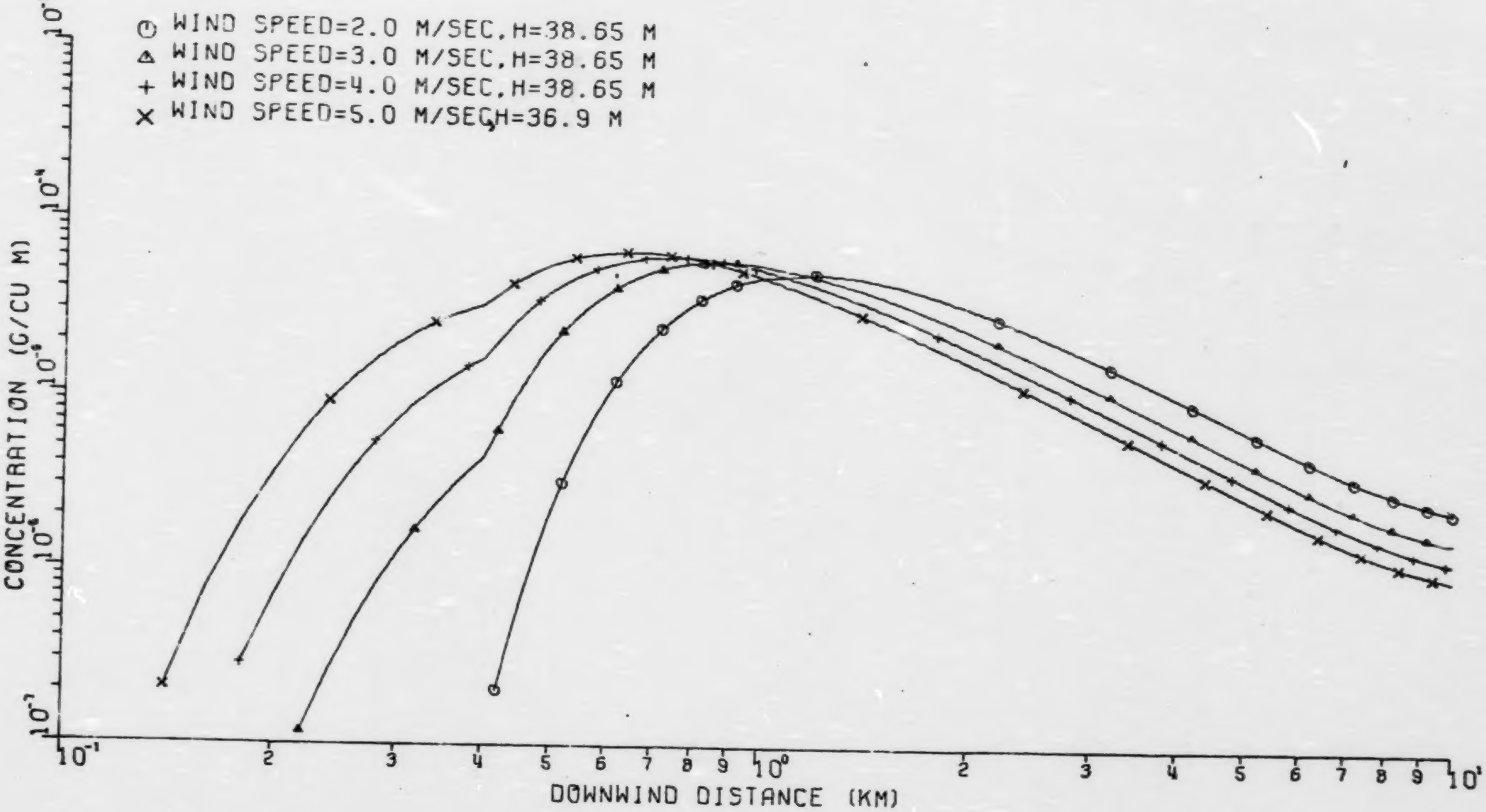

Figure 91. SO_2 concentration versus downwind distance for stability class 2 (plume rise retardation included)

Table 50. ALLOWABLE PARTICULATE EMISSION RATES FOR SPECIFIC FLOW RATES

Effluent flow rate, acfm	Rate of emission, lb/hr
1,000	3.5
2,000	5.3
4,000	8.2
6,000	10.6
8,000	12.6
10,000	14.5
20,000	22.3
40,000	34.2
60,000	44.0
80,000	52.6
100,000	60.4
200,000	92.9
400,000	143.0
600,000	184.0
800,000	219.4
1,000,000	252.0

For a coal-fired power plant the following regulation applies for particulate emissions:

> 105.31 No person may cause, suffer, allow, or permit emissions of particulate matter from any solid fossil fuel fired steam generator to exceed 0.3 lbs. per million Btu heat input maximum 2-hour average.

For the La Palma plant, this translates into an allowable emission rate of 63 lb/hr which is well in excess of the projected value of 15 lb/hr. The Texas SO_2 emission regulation for liquid fuel-fired steam generators states that SO_2 flue gas concentrations may not exceed 440 ppm. This condition will be met for La Palma since the SO_2 flue gas concentration will be about 290 ppm. The regulation for coal-fired plants states that SO_2 emissions shall not exceed 3.0 pounds per million Btu heat input. For the La Palma plant this translates into an allowable emission rate for SO_2 of 627 lb/hr which is well above the projected rate of 135 lb/hr.

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APPENDIX A

PROCESS DESCRIPTION AND EMISSIONS ESTIMATES FOR THE COAL-FIRED CAFB

This section discusses the differences in process operation and emissions associated with the coal-fired CAFB alternative advanced by Foster-Wheeler. Both the 10 MW demonstration plant and 250 MW unit are considered. Operating conditions and emissions will be similar to oil-firing but additional unit operations such as coal crushing and drying and additional problems of ash handling and increased particulate emissions must be considered.

PROCESS DESCRIPTION: 10 MW DEMONSTRATION PLANT

The plant is designed to operate in the same manner as described for oil-firing in Section III. The process flow diagram given in Figure 3 applies to coal-firing as well. Table A-1 is a listing of the mass flow rates associated with coal-firing of the 10 MW demonstration plant.

Coal will be removed from the coal pile and transported to two storage bunkers by a vibrating conveyor. Coal will be withdrawn from the storage bunkers and sent to a crusher to produce a size gradation of 100 percent < 1/2 inch, 88 percent < 1/4 inch, and 18 percent < 30 mesh. Crushed coal will be transferred into a 6-hour intermediate storage silo and withdrawn in two separate streams by gravimetric feeders. The coal will be transported to vibrating tables which are pressurized with flue gas recirculated from the boiler. The solid fuel will then feed into the gasifier through 24 3-inch diameter coal needles, with 12 needles on each side of the gasifier chamber.[1]

Table A-1. MASS FLOW RATES FOR FW 10 MW COAL-FIRED CAFB DEMONSTRATION PLANT

Process stream	Mass flow rate, kg/s	(lb/hr)	Temperature °C	(°F)
1. Limestone to gasifier	0.29	(2,300)		
2. Product gas from gasifier	8.05	(63,800)		
3. Gasifier to regenerator stone transfer	7.94	(63,000)		
4. Regenerator to gasifier stone transfer	7.54	(59,800)		
5. Flue gas to pulsed solid transfer lines				
6. Regenerator off-gas (total)	0.99	(7,820)		
SO_2				
CO_2				
N_2				
7. Water or steam injection				
8. Regenerator off-gas after cyclone and cooling				
9. Coal to RESOX™ reactor	0.09	(730)		
10. Hot solids from RESOX™ reactor	0.03	(260)		
11. Waste solids from RESOX™ quench vessel	0.03	(260)		
12. Hot air to RESOX™ reactor				
13. Influent gas to RESOX™ reactor				
14. Elemental sulfur from RESOX™				
15. Return steam				
16. Water to sulfur condenser				
17. RESOX™ tail gas	1.00	(7,900)		
18. Condensed liquid sulfur	0.05	(390)		
19. Fugitive dust from coal handling system				
20. Air to start up heater				
21. Air to start up heater				
22. Air to RESOX™ reactor				
23. Cooling water for RESOX solid waste				
24. Steam from quench vessel				
25. Regenerator spent solids	0.11	(880)		
26. Regenerator off-gas cycloned solids				

Table A-1 (continued). MASS FLOW RATES FOR FW 10 MW COAL-FIRED CAFB DEMONSTRATION PLANT

Process stream	Mass flow rate, kg/s	(lb/hr)	Temperature °C	(°F)
27. Air to spent solids cooler				
28. Cooled solids				
29. Cooler exhaust to cyclone				
30. Cooled solids to storage				
31. Air emissions from spent solids cooler				
32. Cycloned solids to storage				
33. Solids to storage				
34. Solid waste from storage silo				
35. Air emissions from solids storage silo				
36. Air to gasifier and regenerator				
37. Flue gas recycled from stack				
38. Boiler stack emissions				
39. Flue gas to coal distributing conveyor				
40. Influent gas to gasifier (total)	5.75	(45,600)		
Air	4.07	(32,300)		
Flue gas	0.68	(5,400)		
Tail gas	1.00	(7,900)		
41. Air to regenerator	0.69	(5,500)		
42. Coal to distributing conveyor	2.41	(19,100)		
43. Coal to gasifier	2.41	(19,100)		
44. Oil to gasifier				
45. Fugitive limestone handling emissions				

The remainder of the system including regenerator, RESOX^{TM}, solids handling, and limestone feed is identical to that described for oil-firing in Section III.

EMISSIONS ESTIMATES: 10 MW DEMONSTRATION PLANT

Differences between emissions from coal-firing and oil-firing include air and water emissions from coal handling, an increase in solid waste from ash production, and a potential increase in particulate emissions from the stack.

Emissions from Coal Handling

Coal handling air emissions will emanate from the coal storage pile, coal conveyors and feeders, coal crushers, and coal dryers. Coal drying is not intended for the demonstration plant but is included in the 250 MW proposal and will be discussed in that subsection.

Air emissions from coal storage depend upon wind speed, coal pile surface area, degree of containment, coal density, and the prevailing precipitation-evaporation index. The Midwest Research Institute[2] has estimated a particulate emission factor of 0.018 g/kg (0.0036 lb/ton) which includes losses from coal storage, handling and feeding. Based on an average coal usage rate of 2.4 kg/s (19,000 lb/hr), the particulate emission from coal storage, handling and feeding will be equal to 4.3×10^{-3} g/s (0.034 lb/hr).

Air emissions from coal crushing vary depending on whether the operation is wet or dry and on the type of containment and control practices. There is very limited data available for the prediction of particulate emissions. An uncontrolled emission factor of 0.25 g/kg (0.5 lb/ton) is adapted from estimates for crushing of rock.[3] Coal has different fracturing characteristics than rock but this is the only reasonable estimate of emissions available. Application of this factor results in a particulate emission rate of 0.6 g/s (4.8 lb/hr) from the crushing of coal.

Coal storage drainage depends upon climatological conditions, pile area, and type of coal. Coal pile runoff is generally acidic and contains dissolved solids such as iron, magnesium, and sulfate. Typical values of constituents dissolved in coal pile drainage are given in Table 10. Assuming a storage pile adequate for a 5-day coal supply, a storage pile height of 3.05 m (10 ft), and a yearly precipitation of 0.5 m (20 in.) for the San Benito area, coal pile drainage will be approximately 100 m^3/yr (26,500 gallons per year). Depending on surface drainage characteristics, a portion of this flow will enter groundwater, a portion will evaporate, and the remainder will run off to the Rio Grande or Gulf of Mexico.

Other Emissions

Because of the increased throughput for these unit operations fugitive dust emissions from the RESOX^{TM} system and from the limestone handling system will be slightly greater than that associated with oil-firing of the 10 MW demonstration plant. The particulate emission from RESOX^{TM} coal storage will be 0.16 mg/s (1.3×10^{-3} lb/hr) and emissions from limestone handling will amount to 7.25 mg/s (0.06 lb/hr). Uncontrolled stack particulate emissions will be considerably higher for coal gasification than for oil operation. Actual emission rates will depend upon cyclone design and performance, parameters which are not available at this time. Solid waste problems associated with the 10 MW unit are discussed with the 250 MW commercial unit in a following section.

PROCESS DESCRIPTION: 250 MW COAL-FIRED CAFB

The FW Energy Corporation has developed a preliminary design for operation of a 250 MW coal-fired CAFB power plant based on the design of the 10 MW retrofit demonstration plant. The mass flow rates are higher than those of the oil-fired design because of the lower heating value of coal which equals 6120 kcal/kg (11,020 Btu/lb). The most important pollutants emitted from the plant are particulate air emissions enriched with trace elements and a variety of solid wastes.

A schematic flow diagram of the 250 MW CAFB facility proposed by Foster-Wheeler appears in Figure 4, and associated mass flow rates are listed in Table A-2. The chemistry of the process is as described in Section III. for the oil-fired alternative. This discussion points out the differences in operation during coal-firing.

Coal Storage, Processing, and Feeding

Coal will be delivered to the plant via rail and transported to a storage pile. Working storage will provide a 3-day supply and dead storage will contain a 30-day supply. The coal is then conveyed to a 1-day storage silo from which it is fed to a fluidized dryer in order to assure proper screening and blending properties. During start-up, hot gases for drying will be provided by combusting coal in the furnace section of the dryer. At steady-state operation, hot exhaust from the spent solids cooler will be used for coal drying. Dryer off gas will circulate to a cyclone and scrubber for the removal of particulates and SO_2. Dried coal will then be crushed to yield a gradation of 100 percent < 1/2 inch and 20 percent < 500 μm. Crushed coal will enter two surge bins and exit into two separate blenders for mixing of coal and limestone. Each blender will service one gasifier module consisting of 3 cells per module. Mixed material exiting each blender will be split into three double streams by a vibrating feeder. Each double stream will enter one gasifier cell through 20 injection points per stream. Figure II-3 illustrates this process schematically.

Other Unit Operations

Limestone feeding, gasification and regeneration in the coal-fired 250 MW CAFB are the same as described for the oil-fired version in Section III. The major difference is that coal and limestone are blended prior to feeding the mixture into the gasifier cells. After blending, coal and limestone will be injected into each gasifier cell by two pressurized vibrating conveyors. Forty 3-inch diameter needles will inject the material and serve 0.6 sq m (6.3 sq ft) of floor area each.

Table A-2. MASS FLOW RATES FOR FW 250 MW COAL-FIRED CAFB DESIGN

Process stream[a]	Mass flow rate, kg/s	(lb/hr)	Temperature °C	(°F)
1. Coal from storage to dryer	28.73	(227,800)		
2. Exhaust from dryer to cyclone	0.29	(2,280)		
3. Exhaust from cyclone to scrubber	0.09	(680)		
4. Air emissions from scrubber	0.01	(70)		
5. Solids collected by cyclone	0.20	(1,600)		
6. Coal from dryer to crusher				
7. Fugitive dust emissions from crusher				
8. Coal from crusher				
9. Coal to coal:limestone blenders	28.73	(227,800)		
10. Limestone from storage to dryer				
11. Off-gas from limestone dryer to baghouse				
12. Air emissions from baghouse				
13. Solids collected by baghouse				
14. Limestone to crusher				
15. Fugitive dust emission from limestone crusher				
16. Limestone from crusher				
17. Limestone to gasifier modules	3.91	(31,000)		
22. Limestone and coal from blenders				
23. Limestone and coal from vibrating feeders to gasifier modules				
24. Product gas to quad cyclone	104.4	(827,500)		
25. Product gas to boiler	104.4	(827,500)		
26. Solids returned from quad cyclone				
27. Gasifier to regenerator stone transfer	110.5	(876,000)		
28. Regenerator to gasifier stone transfer	107.4	(851,500)		
29. Regenerator off-gas to twin-cyclones	12.80	(101,500)		

Table A-2 (continued). MASS FLOW RATES FOR FW 250 MW COAL-FIRED CAFB DESIGN

Process stream[a]	Mass flow rate, kg/s	(lb/hr)	Temperature °C	(°F)
30. Spent solids from regenerator	1.32	(10,500)		
31. Regenerator off-gas from twin cyclones	12.80	(101,500)		
32. Regenerator off-gas from cooling	12.80	(101,500)		
33. Air to RESOX™ reactor				
34. Gas to RESOX™ reactor				
35. Coal to RESOX™ reactor	1.24	(9,825)		
36. Solid waste from RESOX™ reactor	0.43	(3,400)		
37. Sulfur gas from RESOX™ reactor				
38. Water to solids quench vessel				
39. Steam from solids quench vessel				
40. Solid waste from quench vessel	0.43	(3,400)		
41. Gaseous effluent from ash storage				
42. Air emissions from ash storage vent filter				
43. Solids from vent filter to ash storage				
44. Solid waste from ash storage				
45. Water to sulfur condenser				
46. Steam from sulfur condenser				
47. Tail gas from sulfur condenser recycled to gasifier	12.96	(102,750)		
48. Liquid sulfur to storage	0.67	(5,175)		
49. Liquid sulfur waste from storage				
50. Solids from regenerator and twin cyclones				
51. Air to solids cooler				
52. Air to spent solids storage				
53. Air to spent solids storage				
54. Solids from solids cooler				
55. Solids to storage				

Table A-2 (continued). MASS FLOW RATES FOR FW 250 MW COAL-FIRED CAFB DESIGN

Process stream[a]	Mass flow rate, kg/s	(lb/hr)	Temperature °C	(°F)
56. Exhaust from solids cooler to cyclone				
57. Cycloned solids cooler exhaust to stack				
58. Cycloned solids cooler exhaust to coal and limestone dryers				
59. Cycloned solids to storage				
60. Solids to storage				
61. Exhaust from storage to vent filters				
62. Air emissions from vent filters				
63. Solids from vent filters to storage				
64. Solid waste from storage				
65. Flue gas from boiler to stack				
66. Air emissions from stack				
67. Flue gas recycled to gasifier	8.92	(70,700)		
70. Air to gasifier	52.93	(419,700)		
71. Air to regenerator	11.04	(87,550)		
72. Liquid waste from coal dryer scrubber	0.63	(5,000)		

[a] Process streams 18 to 21, 68, and 69 are applicable to oil firing and are presented in Section III.

EMISSIONS ESTIMATES: 250 MW CAFB

Emissions from Coal Handling

Air emissions associated with coal handling include storage pile emissions, conveying and feeding emissions, and crushing and drying emissions.

The particulate emission factor for coal piles is taken as 0.0018 g/kg (0.0036 lb/ton) as noted earlier in conjunction with the 10 MW demonstration plant. Two piles will be maintained to provide 33 days of storage. At a coal feed rate of 28.7 kg/s (2730 tons/day), the yearly particulate emission from coal storage, handling and feeding will be 0.052 g/s (3600 lb/hr).

The particulate emission rate for coal crushing is estimated to be 0.25 g/kg (0.5 lbs/ton) of coal processed. At a coal feed rate of 28.7 kg/s (2730 tons/day), the particulate emission from coal crushing at the 250 MW plant will be 7.2 g/s (250 tons/yr).

Air emissions from coal drying are higher than those produced at other points in the coal processing cycle. Table A-3 presents estimates of uncontrolled emissions from three types of coal dryers.

Table A-3. EMISSION FACTORS FOR COAL DRYING

Type of dryer	Uncontrolled emissions,[a] lb/ton
Fluidized bed	20
Flash	16
Multilowered	25

[a] The following collection efficiencies are applicable for control with cyclones:

Cyclone collection efficiency	70%
Multicyclones	85%
Cyclone and wet scrubber	99-99.9%

Exhaust from the coal dryer proposed for the 250 MW installation will pass through a cyclone and scrubber. Therefore, particulate emissions from the drying units can be expected to be on the order of 0.1 g/kg (0.2 lb/ton) of coal processed. This amounts to 2.9 g/s (100 tons/yr) based on a coal feed rate of 28.7 kg/s (2730 tons/day).

A 33-day coal storage requirement is anticipated for the 250 MW plant. Based on an assumed storage pile height of 4.5 m (15 ft) and a yearly precipitation of 0.5 m (20 in), the total runoff from coal storage is approximately 5700 m^3/yr (1,500,000 gallons/yr). The dissolved solid concentrations given in Table 10 will be applicable for the 250 MW proposal.

Other Emissions

Particulate air emissions resulting from RESOX^{TM} coal storage will be approximately 2.19 mg/s (1.7×10^{-2} lb/hr), based on an emission factor of 1.77 μg/kg-yr (0.0036 lb/ton-yr). Emissions from limestone handling will amount to 4.65 g/s (36.9 lb/hr), based on a total particulate emission rate of 1.19 g/kg (2.38 lb/ton). The comments made in the previous section regarding stack particulate emissions from the demonstration plant pertains to the 250 MW unit as well.

Water emissions from the RESOX^{TM} coal storage pile are expected to be the same as calculated for oil-firing of the 250 MW commercial unit and amounts to 212 m^3 (7500 ft^3).

Solid Waste

Coal-fuel operation of the CAFB will result in a larger solid waste output than will oil-fuel operation. This additional material will be produced as bottom ash mixed with spent regenerator stone and as effluents from scrubbers and cyclones used in the coal feed system. The discussion presented below of the environmental impact associated with disposal of this solid waste is based upon the substantial amount of work which has been done on the environmental effects of disposal of solid waste from fluidized bed combustion of coal and from flue gas desulfurization.

Spent solids extracted from the regenerator will have high sulfide and sulfate content. Three predisposal treatment methods are presently being developed, including oxidation and sintering, mixing of stone with coal ash and hot pressing, and wet slurrying. These processes are discussed in some detail in Section IV.

After preliminary treatment of spent stone or ash, three options exist for subsequent handling. The material can be used as landfill, discharged to a holding pond, or recycled. In the first two instances, it is important to assess potential air and water pollutant emissions.

Air emissions will be a problem mainly with landfilling and not with solids discharge to water. In the case of coal ash, it is estimated that wind erosion particulate losses from ash disposal sites will amount to 1 lb/ton of ash discarded. Typical chemical compositions of coal ash are given in Table A-4.[4] Trace elements which may be combined with the ash are listed in Table A-5.[4]

Air emissions from land disposal of spent sorbent stone will consist of particulate matter and gaseous sulfur compounds. The two hazardous compounds of concern are calcium sulfide and calcium sulfate. Sulfide reacts with moisture in the air to form H_2S which is subsequently oxidized to SO_2.

The water environment can be adversely affected regardless of whether spent stone and ash is landfilled or discharged to some type of settling basin. Pollutants are discharged to groundwater and surface waters from landfills by leaching. BCURA[5] and Pope, Evans and Robbins[6] have investigated the properties of the leachate obtained from a fly ash-stone effluent. BCURA found that, although CaO, MgO and CO_3 contents of the leachate varied, all their samples showed common features:

- High pH (10.5 to 11.6)
- High or complete extraction of sulfate
- Negligible extraction of magnesium

Table A-4. POWER PLANT COAL ASH COMPOSITIONS[4]

Constituent	% by weight
Silica (SiO_2)	30-50
Alumina (Al_2O_3)	20-30
Ferric Oxide (Fe_2O_3)	10-30
Lime (CaO)	1.5-4.7
Potassium Oxide (K_2O)	1.0-3.0
Magnesia (MgO)	0.5-1.1
Sodium Oxide (Na_2O)	0.4-1.5
Titanium Dioxide (TiO_2)	0.4-1.3
Sulfur Trioxide (SO_3)	0.2-3.2
Carbon (C) and volatiles	1.0-4.0
Boron (B)	0.1-0.6
Phosphorus (P)	0.01-0.3
Uranium (U) and Thorium (Th)	0.0-0.1

Table A-5. SELECTED TRACE ELEMENTS IN ASH (ppm)[4]

Element	Fly ash[a]	Bottom ash[a]
Arsenic	15	3
Mercury	0.03	< 0.01
Antimony	2.1	0.26
Selenium	18	1
Cadmium	< 0.5	< 0.5
Zinc	70	25
Manganese	150	150
Boron	300	70
Barium	5000	1500
Beryllium	3	< 2
Nickel	70	15
Chromium	150	70
Lead	30	20
Vanadium	150	70

[a] Actual trace element composition will vary widely depending on boiler type and coal composition.

Theis[7] in a study on the potential trace metal contamination of water through fly ash disposal has made the following assertions. At the normal pH range of natural waters, the hydroxide of some metals (Hg, Pb, Cu, Cr, Cd, Zn) controls their solubility. At elevated pH, carbonate may control solubility. In general, trace metals display drastically decreased solubilities with increasing pH. In the pH range 7 to 8.5, only Zn and Cd could be considered soluble. Arsenic is generally very soluble. Theis presented the relationship between solubility and pH. Manlock[5] has also studied leachate solubility-pH relationships.

The elements of major concern are therefore limited to As, Se, V, and Cd. However, since complexes may form which would increase the solubility of the metals, Pb and Hg, at least, may also be of concern in leachates. Theis found for example that addition of EDTA of his ash samples increased the solubility of all elements but mercury.[4]

Rossof and Rossi[6] have investigated possibly toxic elements in scrubber sludges. Although the composition of a scrubber sludge is different than that of the spent stone from a regenerator or overhead from the combustor, in general, the same elements are present and should be affected by pH and ionic species present in a similar manner.

The studies done by BCURA and PER with partially sulfated lime (bed material) have shown that the leachate is highly alkaline. Since metal solubility increases with decreasing pH, however, leaching occurring in an acidic environment will result in higher trace element concentrations. Thus, it is unlikely that the spent stone or overhead will produce an acidic leachate. Increased solubility may, however, occur by means of complex formation. No data were available on complex formation in the leachate from either spent stone or bed material.

Pollutant emissions to the ambient water environment also occur when ash or spent stone is discharged to a settling basin. The overflow from the basin contains a finite percentage of suspended and dissolved solids influent to the basin. It has been estimated that the total suspended solids concentration of ash pond overflow from electric utility power plants averages approximately 100 ng/l.[8]

When coal ash is added to water an immediate reduction in pH and dissolved oxygen occurs.[9] A study by Rohrman[10] indicates that nitrogen and phosphorus are detectable in ash holding basins in dissolved form at a level of 0.1 to 1.0 ng/l. Approximately five times as much phosphorus may be present in suspended form. These nutrients will enhance plant and bacterial growth in the settling pond and may have an effect on ambient water after overflow.

The addition of spent stone to water results in contamination with calcium and magnesium oxide, calcium sulfide, sulfate and carbonate, and magnesium sulfite. This may result in the production of heat, formation of H_2S, and flotation of agglomerated nonsettleable solids.

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APPENDIX B

COMPARISON OF THE CAFB WITH OTHER RESIDUAL OIL UTILIZATION TECHNIQUES

INTRODUCTION

Three alternatives are available for the combustion of high sulfur residual oil in an environmentally acceptable manner:

- In-situ desulfurization
- Precombustion desulfurization of feedstock
- Flue gas desulfurization (FGD).

The CAFB process is the only potentially viable in-situ technique identified by GCA. A number of flue gas desulfurization schemes presently exist which are applicable to both coal-fired and oil-fired boilers. Residual oil desulfurization techniques produce a variety of solid, liquid and gaseous fuels. Of the many desulfurization options, only three are competitive with the CAFB in their ability to handle high metal as well as high sulfur content feedstocks.

The alternative processes are examined in some depth in this and the following two appendices. This appendix is a general overview of desulfurization technology and describes associated unit operations required for sulfur recovery. Flue gas desulfurization (FGD) is presented and existing systems are identified. The final subsections of this appendix compares the environmental impacts of hydrodesulfurization and FGD. Appendix C provides process descriptions and flow charts of potentially viable and currently used individual residual oil desulfurization techniques. Appendix D contains a summary and comparison of the economics associated with all desulfurization options.

RESIDUAL DESULFURIZATION

Present technology has allowed the refiner to produce low sulfur solid, liquid and gaseous fuels from high sulfur feedstocks. For example: coking produces solid, liquid and gaseous fuels; hydrodesulfurization (HDS) produces a liquid fuel; and a procedure called partial oxidation produces a low Btu gas. Although the specific reaction steps vary, most feedstock desulfurization techniques are based on the reaction of hydrogen with oil in the presence of a catalyst, as is shown in the general reaction,

$$\left[\text{fuel sulfur}\right] + H_2 \xrightarrow{\text{catalyst}} H_2S + \left[\text{clean fuel}\right]$$

H_2S is evolved in the desulfurization process. Consequently, residual desulfurization is a two step process: (1) desulfurization of the residual oil with the resulting formation of H_2S; and (2) the disposal or recovery of the H_2S process stream in an environmentally acceptable manner.

The metals content of the feed is the most significant variable influencing processing cost and desulfurization efficiency. High molecular-weight organometallic compounds of vanadium and nickel are found in most crude-oil residues. Under the reaction conditions necessary for desulfurization, some of these complex molecules decompose resulting in the deposition of vanadium and nickel on the surface of the desulfurization catalyst. Over months of continuous operation, metal accumulation causes a reduction in catalytic desulfurization activity. High metals feedstock (metals in excess of 150 to 200 ppm) will, in most cases, require some form of feed demetalization.

In general, residual oils of low to moderate metals content (Ni plus V content less than 100 ppm) and sulfur content as high as 6 percent can be directly desulfurized to yield heavy oil products containing as little as 0.5 wt percent sulfur. For higher metal content feeds and lower sulfur product fuel oil levels, modified techniques, such as Flexicoking or demetalization/desulfurization, will be required.

In addition to the CAFB only three systems (L.C. Fining, demetalization/desulfurization and Flexicoking in conjunction with a HDS unit) have been designed to effectively handle high metal content feedstocks. L.C. Fining and demetalization/desulfurization are both hydrodesulfurization techniques. The Flexicoking process is an extension of the fluid coking process. Process descriptions and flow diagrams of all three processes are found in Appendix C. Other systems are capable of desulfurizing high metal feeds, but at a higher operating cost. Process descriptions of these systems are also presented in Appendix C. The feed to the CAFB will consist of high sulfur and high metal resid, thus this section will compare the CAFB only with those systems capable of handling a similar feed. Economic and process data for all 16 desulfurization techniques considered are presented in Appendix C.

H_2S Removal

Because feedstock desulfurization generates H_2S as a process stream, it is necessary to dispose of or convert this gas to a useful product. The most commonly practiced method is the conversion of H_2S to elemental sulfur by means of a Claus Plant.[3] A flow diagram of a typical two stage Claus sulfur plant is shown in Figure B-1.

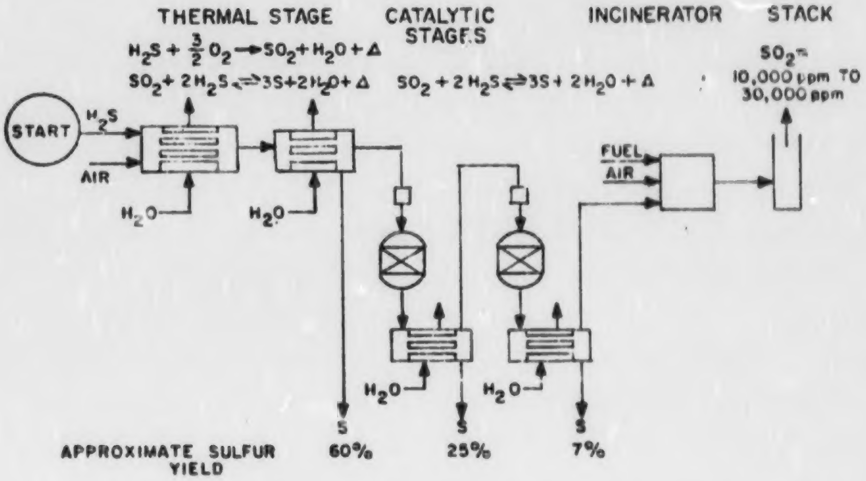
THERMAL STAGE
CATALYTIC STAGES
INCINERATOR
STACK
$H_2S + \frac{3}{2} O_2 \rightarrow SO_2 + H_2O + \Delta$
$SO_2 + 2 H_2S \rightleftharpoons 3S + 2 H_2O + \Delta$
$SO_2 + 2 H_2S \rightleftharpoons 3S + 2 H_2O + \Delta$
SO_2 =
10,000 ppm TO
30,000 ppm
START
H_2S
AIR
H_2O
H_2O
FUEL
AIR
H_2O
H_2O
S
S
S
APPROXIMATE SULFUR YIELD
60%
25%
7%

Figure B-1. Typical two-stage Claus sulfur plant

The most common method of concentrating and collecting H_2S involves washing the product gas with a water solution containing an amine. The rich solution is then steam stripped, driving off the H_2S, and regenerating the absorbing solution. A typical composition of the gas taken from an amine regenerator is:

H_2S	80 - 93%
CO_2	2 - 10%
HC	0.5 - 2%
H_2O vapor	5 - 10%

The H_2S present in the gas may then be converted to elemental sulfur by the following reaction scheme:

$$H_2S + O_2 \rightleftharpoons SO_2 + H_2 \text{ (thermal combustion)}$$

$$2\ H_2S + SO_2 \rightleftharpoons 3\ S + 2\ H_2O \text{ (thermal and catalytic)}$$

$$\text{(overall) } 3\ H_2S + O_2 \rightleftharpoons 2\ H_2O + 3\ S + H_2$$

The overall efficiency of a Claus plant is 90 to 97 percent. Maximum sulfur conversion in a Claus plant is limited because:

- The Claus reaction is reversible and is limited by chemical equilibrium;
- A very significant portion (25 percent) of the sulfur passes through the system in relatively unreduced form - carbonyl sulfide and carbon disulfide.

Claus Tail Gas Cleanup — The tail gas from a typical sulfur plant contains about one-third water vapor, 5 to 15 percent CO_2, 2 to 4 percent sulfur compounds (H_2S, SO_2, COS and CS_2), and the balance nitrogen. The SO_2 concentration in the tail gas is 10,000 to 30,000 ppm. In order to produce a stack gas with less than 250 ppm SO_2 content, the overall sulfur plant must be at least 99.9 percent efficient. This efficiency is not possible with present technology unless a tail gas cleanup plant is also used. Several systems are available for tail gas cleanup: the Beavon Sulfur Removal Process, the Cleanair Sulfur Process, and the IFP process. The investment and operating costs for the Beavon and Cleanair Process are approximately equal to the original cost of the sulfur removal plant. The IFP process is approximately one half the cost of the original sulfur plant but is not as efficient as the first two (99.0 percent versus 99.9 percent).

Beavon Sulfur Removal Process - The Beavon Sulfur Removal Process, developed by Ralph M. Parsons Company and Union Oil Company of California, is capable of limiting SO_2 emissions to 40 to 80 ppm depending on the efficiency of the preceding Claus Plant. In this process the Claus plant tail gas is mixed with hot combustion gas produced by burning fuel gas with air. The resulting reducing mixture is passed through a catalytic reactor similar to that in a Claus plant. The sulfur is hydrogenated to H_2S on a cobalt/molybdate catalyst. Water is condensed from the gas in a heat exchanger. The cooled gas stream is passed to a Stretford section in which H_2S is removed from the gas and converted to elemental sulfur. The cost of this system is approximately equal to the original cost of the Claus plant.

Stretford Process — The Stretford Process consists of a gas washing system wherein the gas is contacted countercurrently with an alkaline washing solution (sodium carbonate). Hydrogen sulfide is removed from the gas stream and is oxidized to elemental sulfur. The sulfur is formed as a finely dispersed solid in the circulating solution. The reduced solution is then oxidized by air blowing which simultaneously removes the sulfur by froth flotation. The oxidized solution is returned to the gas wash system to repeat the cycle. The sulfur slurry is fed to an autoclave where heat is applied to dry and melt the sulfur. Liquid sulfur of greater than 99.5 percent purity is obtained.

Cleanair Sulfur Process — The Cleanair Sulfur Process developed by J.F. Pritchard and Co. and Texas Gulf Sulfur Co. is capable of producing a gas effluent containing less than 250 ppm of SO_2. This system is composed of three process stages, two of which are proprietory and are not fully explained in the literature:

- Stage 1 converts essentially all of the SO_2 to elemental sulfur with some additional conversion of H_2S to elemental sulfur;
- Stage 2, which is the Stretford process (the same process used in the Beavon process) converts the remaining H_2S to elemental sulfur;
- Stage 3 is an important step in controlling COS and CS_2 emissions from the Claus tail gas. Concentrations of these two compounds are reduced to less than 250 ppm equivalent SO_2. Carbon disulfide and carbonyl sulfide are the prime precursors of high SO_2 concentrations in Claus tail gas treating systems.

The cost of this system is similar to the Beavon process and is approximately equal to the original cost of the Claus plant.

IFP Process - The third Claus tail gas treatment process is the Institute Francais du Petrole (IFP) system. Claus tail gas at about 127°C (260°F) is injected into the lower section of a packed tower, where a solvent containing catalyst is circulated countercurrently, resulting in maximum liquid-gas contact. Product sulfur accumulates at the bottom of the tower and is continuously removed. Some solvent is lost by evaporation through the top of the column and therefore must be replaced. Catalyst is also pumped to the tower to maintain a constant concentration. Due to this system's inability to handle COS and CS_2, emissions are approximately 1500 ppm SO_2; however, the original investment is only one-half of that required for the Beavon or Cleanair Sulfur Process.

Flue Gas Desulfurization

Numerous processes have been proposed for flue gas desulfurization (FGD). However, only the six systems outlined in Table B-1 have gained acceptance in the United States. Three more systems are in the prototype stage of development; the Foster Wheeler-Bergbon Forsching process, the Thoroughbred 101 process and the Shell Flue Gas Desulfurization process.

Most FGD systems now in use are operating on coal-fired boilers. Only two plants, the City of Key West, Stock Island Plant and the Boston Edison Mystic 6 Plant (see Table B-2) use FGD on oil-fired boilers. The Stock Island Plant has had considerable difficulty during operation necessitating extensive downtime. The Mystic 6 Plant is the only full size system (a demonstration plant) using magnesia wet-scrubbing on an oil-fired utility generating unit.

Table B-1. SUMMARY DESCRIPTION OF FLUE GAS DESULFURIZATION PROCESSES[4]

Process	Classification/ operating principles	SO_2 particulate efficiency	Development status	Application	Implementation	Advantages	Disadvantages
Lime/limestone scrubbing	Throwaway process/ wet absorption in scrubber by slurry; insoluble sulfites and sulfates disposed of as waste.	Up to 90 percent SO_2 removal/99 percent fly ash removal by most scrubbers.	Most studied but reliability questionable due primarily to scaling; 16 full scale units in operation or planned for start-up by 1977.	Old but preferably new power plants; coal- or oil-fired.	An additional 40 to 60 units forecast for installation by 1977; forecast appears optimistic; 4 to 5 years lead time needed for new plants; 3 years for retrofit of old plants.	Cheapest of existing processes; elimination of particulate control requirement.	Technical reliability doubtful; waste and water pollution problems; reheat of scrubber exit gases needed; supply and handling of large volumes of reactant may be problems.
Double alkali process	Throwaway process/ wet absorption in scrubber; reactants and reaction products soluble; reaction products precipitated and removed from recycled reactant solution outside of scrubber; most common reactant sodium sulfite.	High efficiency > 90 percent SO_2 removal/high particulate removal.	Active area but no full scale demonstration as yet; G.M. installed a unit on a coal-fired boiler in February 1974; several sulfate removal schemes under study.	As above with potentially lower cost and greater ease of operation favoring some inroads into smaller plants.	Research-Cottrell estimates $600 million a year market by 1979; a second generation lime/ limestone system; lead times as above for power plants.	Potentially cheaper, simpler and more reliable than lime/limestone system.	Similar to above and all throwaway systems.
Magnesium oxide scrubbing	Regenerative process/wet absorption by magnesium oxide slurry; fly ash removed prior to or after scrubbing; magnesium oxide regenerated by calcining with carbon; SO_2 by-product can be converted to sulfuric acid or sulfur.	90 percent SO_2 removal/particulate removal as required by prescrubber.	One full scaled unit on test at Boston Edison 150 MW oil-fired unit.	Similar to lime/limestone but oil-fired boilers will not require particulate control upstream of scrubber.	No known plans for immediate implementation; lead times as for lime/ limestone systems.	May be more reliable than lime/limestone process; no known waste disposal problems; regeneration facility need not be located at utility.	Cost of regeneration; marketing of sulfur products; reheat.

Table B-1 (continued). SUMMARY DESCRIPTION OF FLUE GAS DESULFURIZATION PROCESSES[4]

Process	Classification/ operating principles	SO_2 particulate efficiency	Development status	Application	Implementation	Advantages	Disadvantages
Wellman-Lord	Regenerative process/sodium base scrubbing with sulfite to produce bisulfite; regeneration in an evaporative crystallizer; sulfate formed either purged or removed by selective crystallization.	> 90 percent SO_2 removal particulate removal by prescrubber.	Reliably operated (> 9000 hours) in Japan. Full scale demonstration scheduled at Northern Indiana Public Service coal-fired 115 MW boiler; sulfate removal vital to success.	As above.	As above.	More reliable than lime/limestone system based on Japanese experience; simplicity of unit operations in regenerator; waste disposal problems reduced.	Some bleed of solution to remove undesirable reaction products a source of water pollution, otherwise as above.
Citrate system	Regenerative process/flue gas washed to remove particles and SO_3, cooled and absorbed in sodium citrate-citric acid solution in packed tower; solution then reacted with hydrogen sulfide to form sulfur.	> 95 percent SO_2 removal/particulate removal as required.	New development by Bureau of Mines; now testing 1000 cfm pilot plant; also 2000 cfm unit in Terre Haute, Indiana. High potential.	As above.	As above.	High efficiency; economic; no intermediate SO_2 regeneration; high reliability; potentially most attractive of viable processes.	Marketing of sulfur; reheat.
Catalytic oxidation	Regenerative process/catalytic oxidation by V_2O_5 at 850 to 900°F to convert SO_2 to SO_3 followed by condensation to form 70 to 80 percent H_2SO_4. Variation of contact process applied to dilute gases.	85 to 90 percent SO_2 recovery/high particulate efficiency needed to avoid plugging and fouling of catalyst.	Two-year test period on 15 MW boiler; also test on 100 MW boiler of Illinois Power Company; reliability not demonstrated.	New plants, oil or coal.	As above.	Relatively simple and known technology; minimal mechanical operations; no relevant reheat requirements.	Expensive; poor quality sulfuric acid; poor reliability with appreciable downtime; extra ducting to avoid problems associated with ESP failures and high temperature gases.

Table B-2. OIL-FIRED UTILITY BOILERS IN THE UNITED STATES EMPLOYING FLUE GAS DESULFURIZATION

Utility and plant	Capacity, MW	Process type	Startup date	Availability, %	Particulate control		System efficiency		Longest continuous run, days	Comments
					Mech	ESP	Particulate removal, %	SO_2 removal, %		
City of Key West[a] Stock Island[b]	42	Tail-end limestone scrubbing	8/73	Low	—	—	90	85	5	Very little scrubber operation since startup; high liquid level in scrubber causes high pressure drop, which kicks system off-line.
Boston Edison[a] Mystic 6[b]	155	Magnesia scrubbing	4/72	57	No	Yes	—	90	7	Scrubber availability improved from March through June 1974; during this period, the inability to demonstrate runs longer than 7 days was due primarily to boiler problems and not related to scrubber operation; scrubber was shutdown at the end of June at the conclusion of the 2-year test program.

[a] Only oil-fired boilers using flue gas desulfurization.

[b] Oil-fired boiler.

SOURCE: EPRI 209, Status of Stack Gas Control Technology. Prepared by Battelle Columbus Laboratories. July 1975.

ENVIRONMENTAL IMPACTS OF DESULFURIZATION TECHNIQUES

Environmental Impacts of FGD

The environmental impacts of five flue gas desulfurization techniques are discussed below.[5] These techniques are:

1. Limestone slurry scrubbing;
2. Lime slurry scrubbing;
3. Magnesia slurry scrubbing;
4. Sodium solution - SO_2 reduction;
5. Catalytic oxidation

Emissions and effluent data are based on a 500 MW power plant. The fuel is coal containing 3.5 percent sulfur with the FGD system assumed to have a 90 percent efficiency. Coal is used in this comparison instead of residual oil because it is the only fuel with sufficient environmental data for FGD. The solid waste and particulate matter generated when firing residual oil will be less than for coal firing. Table B-3 lists the pollutants which are incompletely converted or generated as byproducts from each system.[5]

Table B-3. FGD ENVIRONMENTAL IMPACT[a] TONS/YR[5]

	Particulate	SO_2	NO_x	Solid waste	Water soluble
Limestone slurry scrubbing	1,280	1,921	448	156,444	-
Lime slurry scrubbing	4,276	1,847	431	156,442	-
Magnesia slurry	1,968	2,884	673	386	110,400[b] (H_2SO_4)
Sodium solution scrubbing	3,077	4,225	1,089	35,002	1,300
SO_2 reduction				(32,700-sulfur)[b]	(Na_2SO_4)[b]
Catalytic oxidation	96	144	34	55	109,900 (H_2SO_4)[b]

[a] Capacity 500 MW; fuel, coal; SO_2 removal, 90%; sulfur in fuel 3.5%.

[b] Salable by-product.

Limestone Slurry Process — A considerable quantity of $CaSO_3/CaSO_4$ solid waste is generated approaching as much as 4 times the weight of the sulfur removed. Wastes discharged to settling ponds are reported to have poor settling properties and may lead to difficulty when reclaimnng the land for future use. Potential runoff from the ponding site could lead to additional water pollution problems.

Lime Slurry Process — Characteristics and problems associated with the lime slurry process are similar in nature to the limestone slurry process. The only difference is that an additional 3000 tons of particulates are produced from the production of lime, which may, however, be generated offsite.

Magnesia Slurry Process — This process is also similar to the two preceding FGD methods with the exception that the by-products ($MgSO_3/MgSO_4$) are regenerated, thus eliminating the large quantities of solid waste. The regeneration step requires additional process water and fuel thus producing additional emissions.

Sodium Solution Process — Although this process is considered to be a regenerative process, a great amount of Na_2SO_4 by-product is produced. This process requires a large amount of steam and water resulting in the largest quantity of airborne pollutants among the five processes.

Catalytic Oxidation Process — This process is the cleanest and least energy intensive of all five processes with no by-products generated other than marketable sulfuric acid.

The only recent data for the environmental impacts of a residual oil-fired boiler using a FGD system is the Boston Edison Mystic 6 Station.[1] This demonstration plant is for a 150 MW magnesia-wet scrubbing system. The design of the facility is based on firing 2.5 percent sulfur fuel. Spent material is sent to an off-site MgO regeneration plant capable of producing

50 tons per day of sulfuric acid. The system is able to recover 91.7 percent of the inlet SO_2 and can control particulate emissions by 57 percent.

Sources of emissions from this demonstration plant include:

- MgO losses (total average loss of 0.37 tons/day over 13 day test program)
  - Stack
  - Centrifuge washing
  - Centrifuge case leaks
  - Pump packing gland leaks
  - Absorber overflow
  - MgO slurry tank blow-down
  - MgO slurry tank overflow
  - Centrate tank overflow
  - Solids loss at dryer feed end
  - Dust losses at dryer I.D. fan
  - Dust loss at expansion joints
  - Spillage at MgO feeder
  - Spillage at $MgSO_3$ belt galley
  - Spillage at truck loading point
- Waste water
  - Process water
  - Cooling water
- Solids buildup in regenerated MgO
  - Vanadium
  - Nickel
  - Ash

Environmental Impacts of Residual HDS

Possible environmental problem areas from HDS are:

- Catalyst disposal (including vanadium and nickel deposits)

- Vanadium, nickel and other trace constituents in desulfurized fuel
- Various waste water streams
- Claus and tail gas cleanup emissions
- NH_3 from amine scrubber
- Catalyst disposal from Claus and tail gas cleanup process
- COS emissions
- CS_2 emissions

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2. Keairns, D.L., D.H. Archer, R.A. Newby, E.P. O'Neill, and E.J. Vidt. Evaluation of the Fluidized-Bed Combustion Process. Volume IV — Fluidized-Bed Oil Gasification/Desulfurization. Westinghouse Research Laboratories, Pittsburgh, Pa. U.S. Environmental Protection Agency, Research Triangle Park, N.C. Report Number EPA-650/2-73-048d. December 1973. 328 p.

3. Beers, W.D. Characterization of Claus Plant Emissions. Process Research, Inc., Cincinnati, Ohio. U.S. Environmental Protection Agency. Report Number EPA-R2-73-188. April 1973. 173 p.

4. Surprenant, N.S., R. Hall, S. Slater, T. Suza, M. Sussman, and C. Young. Preliminary Emissions Assessment of Conventional Stationary Combustion Systems. Volume II — Final Report. GCA Corporation, GCA/Technology Division, Bedford, Mass. U.S. Environmental Protection Agency, Research Triangle Park, N.C. Report Number EPA 600/2-76-046b. March 1976. 531 p.

5. Yan, C.J. Evaluating Environmental Impacts of Stack Gas Desulfurization Processes. Environ Sci Technol. 10:54-58, January 1976.

APPENDIX C

PROCESS DESCRIPTIONS AND FLOW DIAGRAMS OF RESIDUAL OIL DESULFURIZATION TECHNIQUES

FLEXICOKING [1-4]

Flexicoking is the advanced EXXON fluid coking process with coke gasification. It produces very low sulfur fuel oil blendstocks (0.4 wt percent) from a wide range of residuum feeds. About 99 percent of a typical vacuum residuum is converted to liquid and gaseous fuel products and about 95 percent of the total sulfur in the residuum feed is removed and recovered as elemental sulfur. The remaining 1 percent feed is then converted into a low-sulfur coke purge containing the bulk of the metals contained in the feed. Approximately 50 percent of the combined nitrogen in the feed is converted to N_2.

Process Description

The flow diagram of a Flexicoker unit is shown in Figure C-1. Vacuum residuum is cracked at 482 to 538°C (900 to 1000°F) and about 1.7 bar (10 psig) in a fluidized coke bed, yielding a wide range of gaseous and liquid products plus coke. Vapor products leave the reactor and are quenched in a scrubber where entrained coke is removed and a heavy recycle feed is condensed. The final hydrocarbon products are then separated in a conventional fractionator.

In the Flexicoking process, coke from the conventional coker reactor circulates through the heater vessel and gasifier where the coke is gasified by steam and air or oxygen. The heat required for the residuum cracking

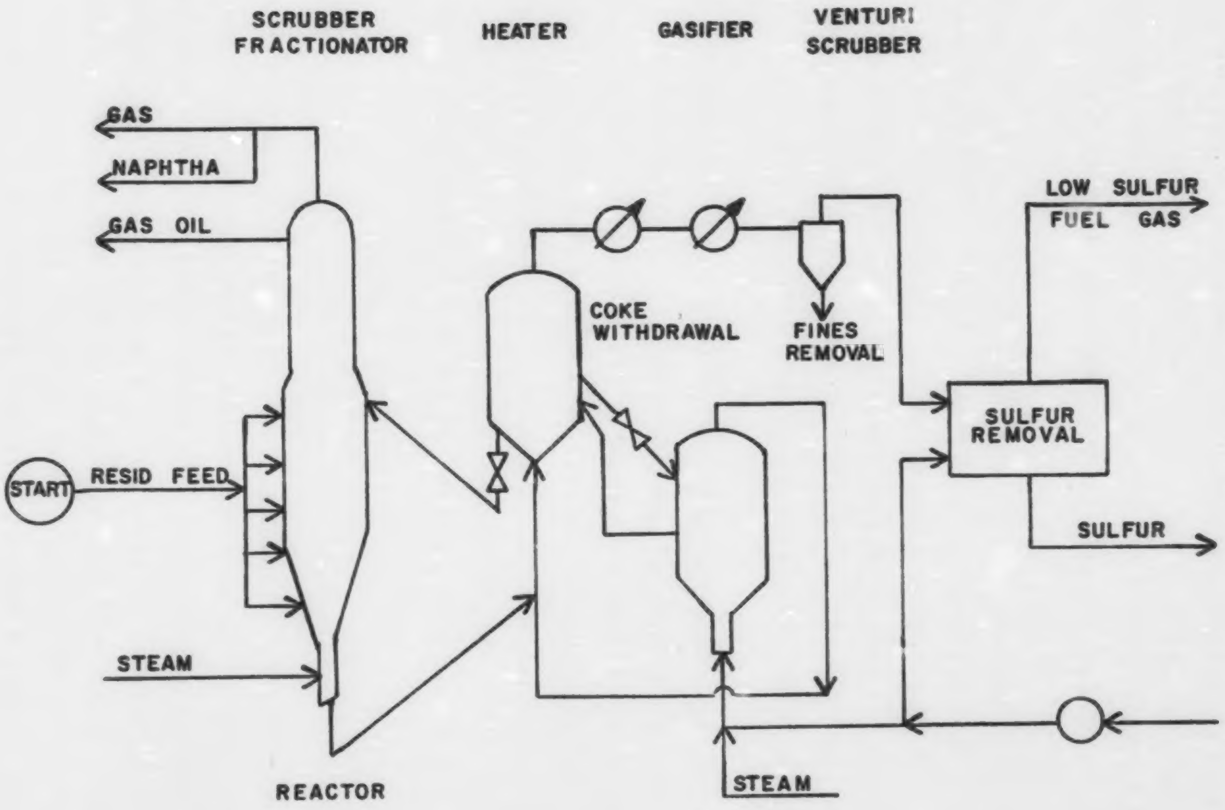

SCRUBBER FRACTIONATOR
HEATER
GASIFIER
VENTURI SCRUBBER
GAS
NAPHTHA
GAS OIL
START
RESID FEED
STEAM
REACTOR
COKE WITHDRAWAL
FINES REMOVAL
SULFUR REMOVAL
LOW SULFUR FUEL GAS
SULFUR
STEAM

Figure C-1. Flexicoking unit

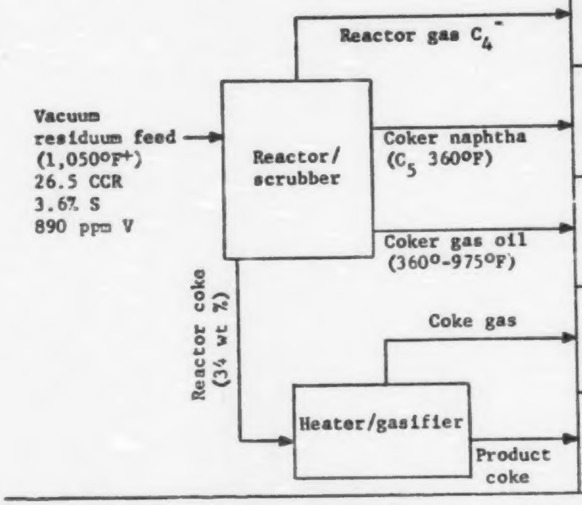
reaction is supplied by the sensible heat removed from the gasifier product gas and the hot solids stream circulating between the gasifier and heater. The hot product gas is then cooled in a waste heat boiler, scrubbed to remove fines and desulfurized. The fines are a metals-rich residue, containing 99 percent of the metals in the feed, and are thus a potentially valuable by-product for sale to the metallurgical industry.

About 20 to 25 percent of the total feed sulfur is liberated as H_2S in the reactor and appears in the off gas. Essentially all of the H_2S is removed from this gas by amine scrubbing. Over 90 percent of the sulfur present in the liquid products, amounting to 40 to 45 percent of the total sulfur in the feed, is removed by hydrotreating. The remaining 30 to 40 percent of the feed sulfur is concentrated in the reactor coke.

In the heater/gasifier the majority of coke-sulfur is gasified with the coke. About 97 percent of the coke-gas sulfur will be present as H_2S which can be removed by commercially available processes (e.g., a Claus plant). The total sulfur content of the resulting fuel gas can easily be reduced to about 250 ppm, which is equivalent to a 0.3 wt percent sulfur fuel oil. The remainder of the coke sulfur, less than 1 percent of the feed sulfur will be found in the solids purge (see Figure C-2).

Stage of Development

Exxon Research and Engineering Company has recently operated the world's first Flexicoker. It is rated at 750 bbl/day and converts vacuum residue and tar materials into liquid and gaseous products. Although it is not of commercial scale, it is larger than a conventional pilot-plant. As of March 1975 the unit had been operated for approximately 6 months. The first commercial Flexicoker, rated at 22,000 bbl/sd is under construction at Toa Oil Company's Kawashi refinery in Japan. It is due for start-up the first quarter of 1976.


Vacuum residuum feed (1,050°F+) 26.5 CCR 3.6% S 890 ppm V
Reactor/ scrubber
Reactor gas C4-
Coker naphtha (C5 360°F)
Coker gas oil (360°-975°F)
Reactor coke (34 wt %)
Heater/gasifier
Coke gas
Product coke

Yield on feed	% feed sulfur in product	Product qualities	Possible disposition
13 wt %	25	7%/Nil S[a] 1,300 Btu/scf	• Refinery fuel • LP-gas recovery • H_2 manufacture
10 wt %/15 vol %	~2	0.7% S/<0.07% S[a]	• Refinery fuel • MO gas blending • SNG manufacture
44 wt %/48 vol %	36	3.1% S/<0.3% S[a] ~15 API <5 ppm vanadium	• Low S fuel sales • Further conversion to MO gas or distillates
0.2 FOEB/bbl feed	36	<170 ppm S[b] 125 Btu/scf (low NO_x)	• Refinery fuel or sales to local consumer
1.5 wt %	~1	~6% vanadium <2% sulfur	• Feed for metals recovery • Fuel

---

[a] Sulfur shown before and after desulfurization based on typical % desulfurization in downstream processing facilities; up to 98% of S in feedstock can be recovered.

[b] The coke gas can be desulfurized to less than 170 ppm (0.2 wt % S equivalent fuel oil).

Figure C-2. Flexicoking products[1]

Economics

The economics of the Flexicoking process are presented in Table C-1.

Table C-1. ECONOMICS OF FLEXICOKING PROCESS

Investment, battery limit onsite, (Basis: Direct material and labor 2nd quarter 1973 U.S. Gulf Coast), $ per bpsd capacity	650-800[a]
Typical requirements, units/bbl, feed:	(140-180)
Steam export, (600 psig), lb	(140-180)
Steam required, (150 psig), lb	50-70
Electricity, kwh	14-18
Water, cooling, gal	8.10
Water, boiler feed, gal	20-30
Air, scf	12-16

[a] Updated economic data are presented in Appendix D.

GULF HDS[3,5-8]

The Gulf Hydrodesulfurization (HDS) process can upgrade high sulfur atmospheric residuum to low sulfur fuel oil, to minor amounts of low sulfur naphtha, and to middle distillate. Several different crudes have been charged to commercial units either individually or as mixtures. A listing of these crudes is presented in Table C-2. The Gulf HDS process offers the flexibility of producing a wide range of low sulfur products (0.1 to 1.0 wt percent) depending upon the number of catalytic reactors installed in the system. A one reactor system (Type II) using Kuwait 53 percent reduced crude can produce a product with 1 percent sulfur, a two reactor system (Type III) can produce a 0.3 percent product and a three reactor system (Type IV) can produce a product with 0.1 percent sulfur.

Table C-2. REDUCED CRUDES TO HDS UNITS

Crudes charged (separately or in mixtures) to commercial units:

Kuwait
Murban
Nigerian
Forcados
Iranian Heavy (20%)
Sumatra
Arabian Light

Additional possible crudes that could be charged include:

West Texas
Arabian Medium
Arabian Heavy
Safaniya
Zubair
Darius
Kirkuk
Ratawi
Khafji
Iranian Light
Rostam
Alaskan

Process Description

A process diagram of the Gulf HDS Unit is shown in Figure C-3. The second and third reactors are present depending on the percent sulfur desired in the final product. The reactor charge consists of fresh filtered feed from a desalted crude, recycle gas and makeup hydrogen. This mixture is heated to 343 to 454°C (650 to 850°F) prior to entering the reactor. Hydrogen rich gas from the reactor is flashed into a high presuure separator. The separator gas is purified prior to being recycled back to the reactor. The liquid bottoms from the high pressure separator pass through a low pressure separator to remove H_2S and fuel gas. The remainder enters a fractionator for the separation of naphtha, middle distillate and fuel oil.

Economics

Economic data shown in Table C-3 are based on Kuwait 53 percent reduced crude.

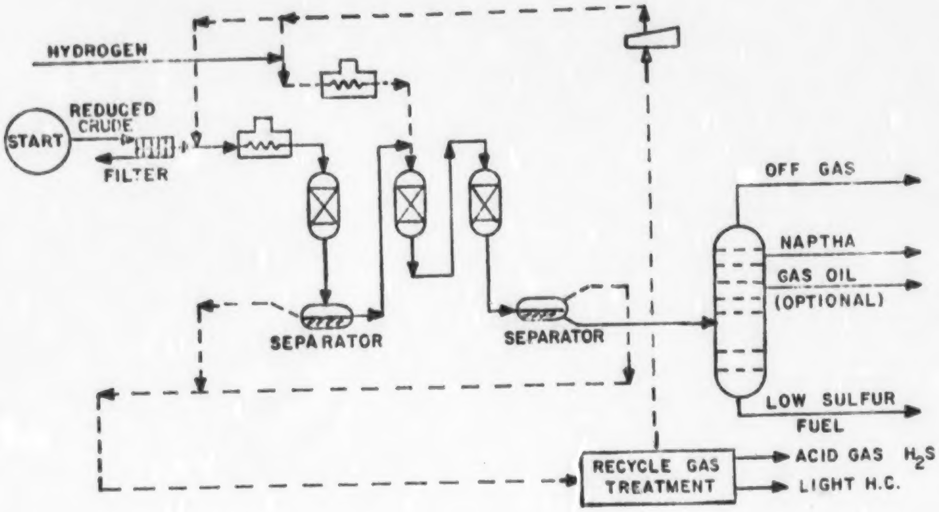

HYDROGEN
REDUCED CRUDE
START
FILTER
SEPARATOR
SEPARATOR
OFF GAS
NAPTHA
GAS OIL (OPTIONAL)
LOW SULFUR FUEL
RECYCLE GAS TREATMENT
ACID GAS H_2S
LIGHT H.C.

Figure C-3. The Gulf HDS process — Type IV process uses three reactors whereas Type II uses only the first and Type III uses the first two

Table C-3. ECONOMICS OF GULF HDS

Type unit	II	III	III	IV
% Feed sulfur	1.0	0.5	0.3	0.1
Typical requirements[a] (Basis: 50,000 bpsd)				
Unit cost, U.S. Gulf Coast, $ MM	21	27		32
Hydrogen consumption, scf/bbl feed	515		740	900
Utilities, average				
Power shaft, kW	12,300		16,500	17,500
Steam, 50 psig, M lb/hr	67		75	81
Fuel, MM Btu/hr	140		190	190
Water, cooling, 20 F rise, gpm	5,200		6,200	6,200
Condensate, gpm	50		65	65

[a] Cost estimates as published May 1973 — updated economic data are presented in Appendix D.

Stage of Development

The development of the Gulf HDS process is presented in Table C-4.

Table C-4. DEVELOPMENT OF GULF HDS

Company	Nippon Mining	Idemitsu	Okinawa	Mitsubishi Oil
Date on-stream	12/22/69	3/5/72	4/26/72	Under construction
Type unit	I	II	II	II
Charge stock (design)	Kuwait reduced crude			
Charge capcity, bpsd	28,000	40,000	38,000	45,000
Fuel oil product sulfur, wt %	1.0	1.0	1.2[a]	1.0
Cycles per year	2	2	2	1

[a] Design charge is 800°F+ (38%) Kuwait reduced crude. When charging 650°F+ Kuwait reduced crude, fuel oil product sulfur is 1.0 percent.

RCD ISOMAX[3,9-12]

In the RCD Isomax process residual oils of low to moderate metals content (nickel and vanadium content less than 100 ppm) and sulfur as high as 5 to 6 wt percent are desulfurized directly to yield a heavy fuel oil product containing as little as 0.3 wt percent sulfur. Yields for RCD Isomax processing of Kuwait reduced crude to 1, 0.7, and 0.3 wt percent sulfur are shown in Tables C-5, C-6, and C-7.

Table C-5. YIELDS FOR RCD ISOMAX PROCESSING OF KUWAIT REDUCED CRUDE TO 1.0 WT PERCENT SULFUR

	Wt - %	LV - %	°API	S, wt - %
Feed oil	100.00	100.00	16.3	3.92
Chem H_2 (scfb)	0.95	(600)		
NH_3	0.09			
H_2S	3.14			
C_1	0.23			
C_2	0.09			
C_3	0.10			
C_4	0.06	0.1		
C_5 - 400°F	1.64	2.0	51.2	0.01
400°F$^+$	95.60	99.6	22.4	0.95
Total	100.95	101.7		

Table C-6. YIELDS FOR RCD ISOMAX PROCESSING OF KUWAIT REDUCED CRUDE TO 0.7 WT PERCENT SULFUR

	Wt - %	LV - %	°API	Sulfur, wt - %	Nitrogen, wt - %	Viscosity, cst @ 122°F
Feed oil	100.00	100.00	15.8	4.1	0.23	330
Chem H_2 (scfb)	0.98	(614)				
NH_3	0.11					
H_2S	3.83					
C_1-C_4	0.45					
C_5 - 400°F	1.10	1.35	58.9	0.01		
400°F$^+$	95.49	99.51	22.1	0.71	0.19	74
Total	100.98	100.86				

Table C-7. YIELDS FOR RCD ISOMAX PROCESSING OF KUWAIT REDUCED CRUDE TO 0.3 WT PERCENT SULFUR

	Wt - %	LV - %	°API	Sulfur, wt - %	Nitrogen, wt - %	Viscosity, cst @ 122°F
Feed oil	100.00	100.00	15.8	4.1	0.23	330
Chem H_2 (scfb)	1.18	(750)				
NH_3	0.13					
H_2S	4.06					
C_1-C_4	0.89					
C_5-400°F	2.61	3.30	55	0.01		
400°F	93.49	98.69	24.0	0.3	0.13	50
Total	101.18	101.99				

Process Description

A schematic flow diagram of a typical RCD Isomax process is shown in Figure C-4. The basic elements employed in this process are similar to those used in many distillate hydrodesulfurization units.

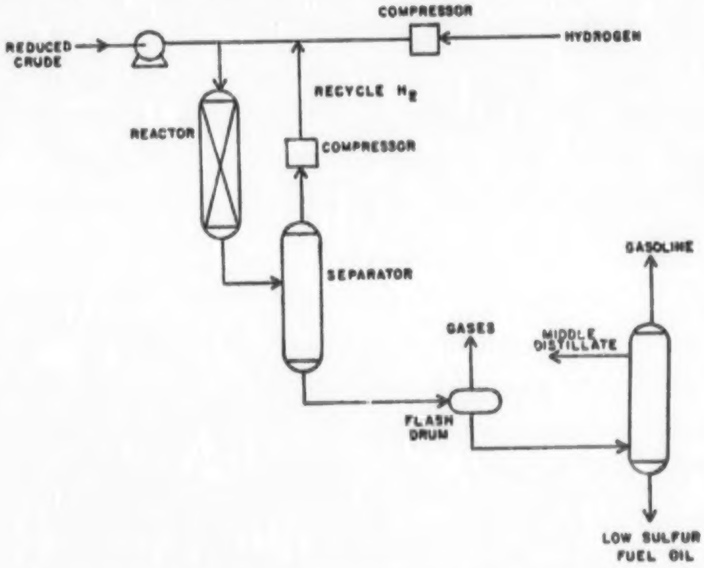

COMPRESSOR
REDUCED CRUDE
HYDROGEN
RECYCLE H_2
REACTOR
COMPRESSOR
GASOLINE
SEPARATOR
GASES
MIDDLE DISTILLATE
FLASH DRUM
LOW SULFUR FUEL OIL

Figure C-4. Typical RCD Isomax unit flow diagram

Reduced crude, makeup and recycle hydrogen are pretreated prior to entering the RCD reactor. Depending on the design, multiple series flow and/or multiple reactor trains may be used. Reactor effluent is cooled and directed to a high pressure separator where recycle hydrogen and a liquid product are recovered. Separator liquid is sent to a low pressure flash drum where the major portion of dissolved hydrogen and light co-product gases are flashed off. The flashed liquid is charged to a fractionator for separation into individual products or sent to a product stripper for flash point control without separate recovery of distillate product.

Stage of Development

As of September 1974 three RCD Isomax units were on-stream and two others were being designed. Total capacity of the five units is 175,000 bpsd.

Economics

The economics of the RCD Isomax process are presented in Table C-8.

RESIDUE DESULFURIZATION (BP PROCESS)[13,14]

The British Petroleum Company has developed a process to reduce the sulfur content of Kuwait atmospheric residue from 4 to 1 wt percent. A 50,000 bbl/sd unit has been designed with the following goals:

- High desulfurization activity;
- High tolerance to metals accumulation;
- Low cracking activity to give high fuel-oil yields;
- Low denitrogenation activity;
- Low hydrogen consumption;
- Low catalyst cost.

Table C-8. ECONOMICS OF RCD ISOMAX PROCESS[a]

Basis: 50,000 bpsd charge
330 operating days per year
Utility values: Electricity 1¢ kWh
Fuel 42 ¢ MM Btu
Cooling water 2 ¢ /1,000 gal
Steam, 73 ¢ /1,000 lb

	1% sulfur in product		0.3% sulfur in product	
Investment, 10^6 $	21.0		31.0	
Operating costs	$/SD	¢/bbl	$/SD	¢/bbl
Direct operating costs				
Labor	624	1.2	772	1.5
Utilities	5,146	10.3	5,428	10.9
Catalyst and royalties	3,150	6.3	4,511	9.0
Maintenance, taxes and insurance @ 6% of plant cost	3,818	7.6	5,636	11.3
Subtotal	12,738	25.4	16,347	32.7
Indirect operating costs				
Administrative at 100% of labor	624	1.2	772	1.5
Interest and depreciation 8%, 10 years	10,062	20.1	14,853	29.7
Subtotal	10,686	21.3	15,625	31.2
Total operating costs, ex. 11	23,424	46.7	31,972	63.9
Hydrogen, at 60¢/Mcf	21,000	42.0	27,000	54.0
Grand total	44,434	86.7	58,972	117.9

[a] Economic data published May 1973 — updated economic data are presented in Appendix D.

Process Description

A flow diagram of the BP Residue Desulfurization process is shown in Figure C-5.

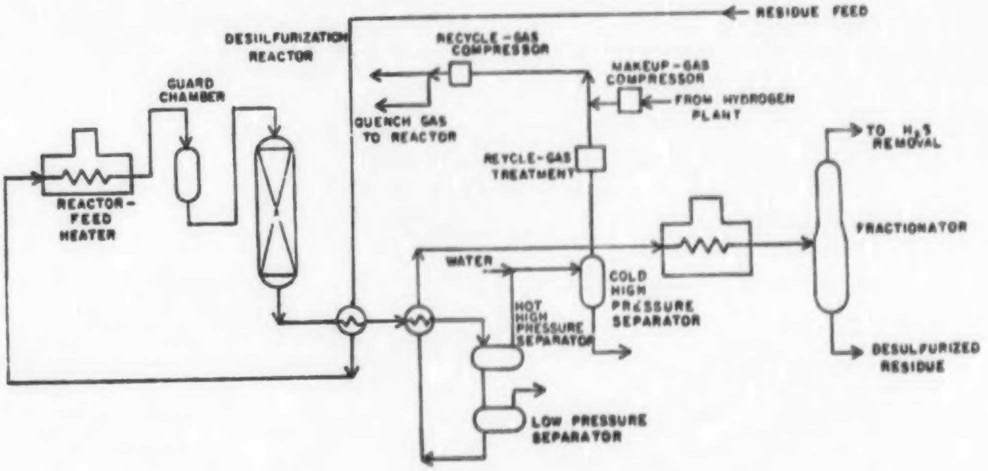

RESIDUE FEED
DESULFURIZATION REACTOR
RECYCLE-GAS COMPRESSOR
MAKEUP-GAS COMPRESSOR
FROM HYDROGEN PLANT
GUARD CHAMBER
QUENCH GAS TO REACTOR
TO H_2S REMOVAL
REYCLE-GAS TREATMENT
REACTOR-FEED HEATER
FRACTIONATOR
WATER
COLD HIGH PRESSURE SEPARATOR
HOT HIGH PRESSURE SEPARATOR
DESULFURIZED RESIDUE
LOW PRESSURE SEPARATOR

Figure C-5. BP Residue Desulfurization process

Atmospheric residue feed and hydrogen-rich recycle gas are brought to the required reaction temperature and are passed through a guard chamber prior to entering the main reactor. Recycle gas is also sent to the main reactor as a quench.

The reaction effluent passes to a separation system and the liquid products are recovered by distillation. To prevent the deposition of ammonium sulfide, water is injected into the recycle gas stream. The recycle-gas treatment process involves the partial removal of methane and hydrogen sulfide necessary for maintaining an adequate hydrogen partial pressure in the reaction section.

Stage of Development

As of 1971 several pilot plant tests had been performed. Typical product yields obtained at catalyst mid-life are shown in Table C-9. The catalyst used in this process was selected not on the basis of regenerability but rather on its ability to maintain selective desulfurization activity, its low cost and its high tolerance for metals deposition.

Table C-9. PILOT-PLANT DATA

	Filtered feed	Total fuel-oil product, > 177°C
Yield on feedstock, wt %		96.73
Yield on feedstock, vol %		99.74
Specific gravity, 60/60°F	0.955	0.915
Flash point, °F	245	245
Sulfur content, wt %	3.87	0.96
Viscosity kinematic at 50°C centistokes	220	55
Viscosity kinematic at 60°C centistokes	126.3	35.5
Viscosity kinematic at 77°C centistokes	57.2	19.6
Viscosity kinematic at 99°C centistokes	26.1	10.7
Pour point, °F	65	45
Conradson carbon residue, wt %	9.3	4.5
Asphaltenes, wt %	2.2	0.7
Ash content, wt %	0.010	0.001
Iron content, ppm	3	3
Vanadium content, ppm	48	10
Nickel content, ppm	16	5
Sodium content, ppm	17	6
Nitrogen content, ppm	1,975	1,555
Desulfurization, wt %	75	75
Demetalization (V + Ni only), wt %	77	77
Denitrogenation, wt %	21	21

Economics

The economics of the BP process are presented in Table C-10.

Table C-10. ECONOMICS OF BP PROCESS

	Feed	Products > 350°F		
Sulfur content, wt %	4.0	1.0	0.5	0.3
Yields, vol %				
Light gasoline (C_5-180°F)		0.4	0.6	1.0
Heavy gasoline (180-350°F)		0.6	1.	2.8
Kerosene (350-438°F)		1.5	1.9	4.1
Gas oil (438-626°F)	4.6	10.5	11.0	13.9
Fuel oil residue (> 626°F)	95.4	88.7	87.8	81.3
Total	100.0	101.7	102.4	103.1
Chem H_2 consumption, scf/bbl		625	835	1050
Investment (Basis: 50,000-bpsd unit to desulfurize Kuwait atmospheric residue, estimated erected cost - materials and direct labor - mid 1973. U.K. location, excluding initial catalyst charge), $ per bbl charge		355	410	
Operating cost (exluding capital charges and allowing no credits for recovered sulfur or distillate produced), $ per bbl fuel oil[a]		1.15	1.50	1.90

[a] Based on hydrogen at $1 per 1,000 scf and fuel at $1.50 per MM Btu — updated economic data are presented in Appendix D.

RESID HYDROPROCESSING (STANDARD OIL CO. INDIANA)[15,16]

A fixed bed catalytic hydrodesulfurization process developed by the Standard Oil Company of Indiana uses a proprietary catalyst that resists poisoning by sulfur, nitrogen, metals, coke-forming materials and other troublesome constituents of resids. Typical feedstocks consist of atmospheric and vacuum resids from Khafji, Gach Saran, Cyrus, Jobo, Darius, El Morgan, Kuwait, West Texas and Mid-Content crudes. Low sulfur fuels ranging upward from about 0.3 percent sulfur can be obtained from these crudes. The catalyst utilized in the process enables desulfurization to be carried out at large hydrogen partial pressures and low catalyst usage. The catalyst is also highly tolerant to metal contaminants and is specifically designed to overcome pressure drop problems. Table C-11 presents yield data for four types of resid feeds.

Process Description

A process diagram of the hydrodesulfurization process is shown in Figure C-6. Makeup recycle hydrogen is combined with resid feedstock prior to entering a prereaction furnace. Heated material from the furnace passes through the multibed reactor and then into a high pressure separator where vapors are separated from the liquid. The bottoms from the high pressure separator are further processed in a low pressure separator, where additional liquid and vapor streams are generated. The vapor streams from both separators are scrubbed for H_2S removal and are used as recycle gas in the reactor. The hydrocarbon liquid streams from the two separators are fractionated into desulfurized resid and lighter products. The desulfurized resid can be blended with other fuels or processed further to recover gas oil.

Economics

The economics of the hydrodesulfurization process are presented in Table C-12.

Table C-11. HDS YIELD DATA

	Kuwait		Sour West Texas		Khafji	Gach Saran
Charge (atm. resids)						
^{o}API	15.1		15.4		12.3	14.6
Sulfur, wt %	4.02		3.65		4.47	2.55
Ni + V, ppw	69		41		141	258
Viscosity, cs at 122^{o}F	400		300		3,000	650
Pour point, ^{o}F^{-}	55		80		70	75
Vol. % 650^{o}F^{-}	0		13.3		0	0
Yields (average)						
H_2 consumption, SCFB	560	600	700		780	400
C_1-C_4, wt %	0.46	0.87	1.4		0.70	0.80
C_5-360^{o}F, vol %	1.4	1.9	3.0		2.2	2.4
360-650^{o}F, vol %	8.7	11.7	26.8		10.9	11.8
650^{o}F^{+}, vol %	91.0	88.0	72.1		89.5	88.0
Gas oil, vol %			57.1			
Residuum, vol %			15.0			
Product quality, 650^{o}F^{+}			Gas oil	DeS. resid		
Sulfur, wt %	1.0	0.5	0.23	0.7	0.65	0.40
^{o}API	19.9	21.4	24.8	9.8	20.5	20.5
Ni + V, ppm	16	9	0.1	31	57	67
Viscosity, cs at 122^{o}F	270	140	72	80[a]	270	260
Pour point, ^{o}F	25	25	100	155[b]	60	65
Ramscarbon, wt %			1.0	16		

[a] At 250^{o}F.

[b] Softening point.

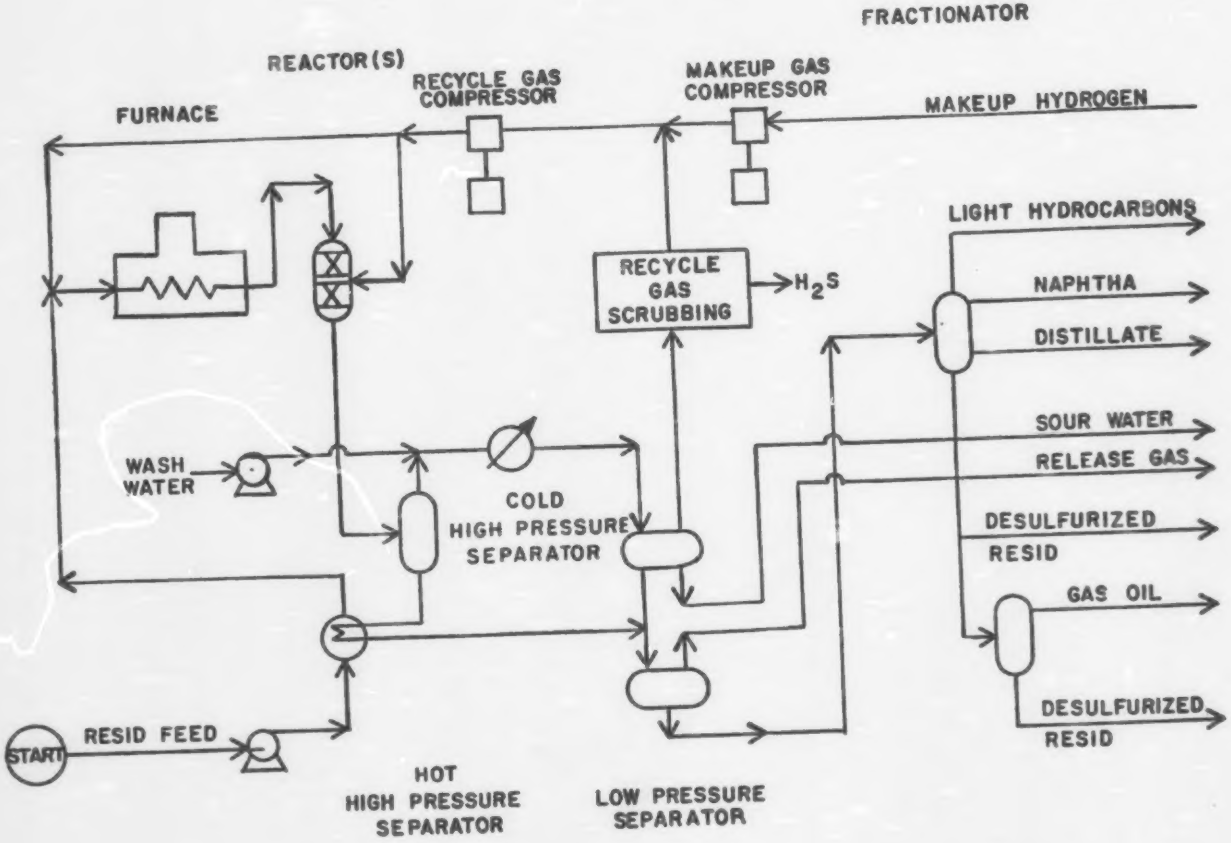

FRACTIONATOR
REACTOR(S)
RECYCLE GAS COMPRESSOR
MAKEUP GAS COMPRESSOR
FURNACE
MAKEUP HYDROGEN
LIGHT HYDROCARBONS
RECYCLE GAS SCRUBBING
H_2S
NAPHTHA
DISTILLATE
SOUR WATER
WASH WATER
RELEASE GAS
COLD HIGH PRESSURE SEPARATOR
DESULFURIZED RESID
GAS OIL
DESULFURIZED RESID
START
RESID FEED
HOT HIGH PRESSURE SEPARATOR
LOW PRESSURE SEPARATOR

Figure C-6. Resid Hydroprocessing - Standard Oil Co., Indiana

Table C-12. ECONOMICS OF HDS PROCESS[a]

Investment,[b] (Basis: desulfurizing 20,000 to 40,000 bpsd of Kuwait atmos. resid to 1.0 wt % sulfur in 650°F+ product, January 1973, Gulf Coast), $ per bpsd capacity	560-620
Typical requirement, unit per bbl feed	
Electricity, kWh	4.4
Steam, lb	2.6
Fuel, M Btu	86
Water, cooling, gal	160
Water, process gal	4.2
Catalyst $	0.08
Average hydrogen consumption scf	560

[a] Includes amine recovery and regeneration.

[b] Updated economic data are presented in Appendix D.

LC-FINING[10,15,29]

The LC-Fining process can be used for the desulfurization of atmospheric residuum, vacuum bottoms and other heavy oils. Efficient hydrocracking is employed to convert heavy gas oils or residues into lighter fractions.

Process Description

Hydrogen and heavy oils are reacted in a fluid bed consisting of vapor and liquid in which solid catalyst particles are maintained in random motion by continuous upflow of the liquid phase. Two types of catalyst can be used, a 1/32-inch extrudate or a fine powder. The extrudate form requires an internal liquid recycle to expand the catalyst bed. The powder form is fed into the reactor mixed with the fuel oil and does not require the internal pumped liquid recycle for fluidization. At equilibrium operation, catalyst leaving the reactor with the fuel product is replaced by adding catalyst with the feed. Catalyst replacement is done on a daily basis. Because the bed is in a continuous motion, contact between the catalyst and the oil is greatly improved, resulting in longer catalyst life and the capability to process high metals feedstock. Figure C-7 is a schematic of the LC-Fining process.

Stage of Development

The development of the LC-Fining process is presented in Table C-13.

Table C-13. DEVELOPMENT OF LC-FINING PROCESS

Commercial installations

Unit	Capacity, bpsd	Status	Years
Lake Charles, La.	6,000	In operation	12
Shuaiba, Kuwait	28,800	In operation	7
Salamanca, Mexico	18,500	In operation	2
Lake Charles, La.	25,000	In design	
Kashima, Japan	10,000	In design	

Economics

The economics of the LC-Fining process are presented in Table C-14.

RESID ULTRAFINING[3,19]

A proprietary process developed by Amoco, called Resid Ultrafining, has been used to desulfurize numerous resids of widely varying properties in both bench scale and large pilot plant equipment.

Process Description

Resid feed is preheated then combined with recycle hydrogen and heated to reactor inlet temperature in a furnace (see Figure C-8). Desulfurization takes place in a multibed reactor where an intermediate gas quench

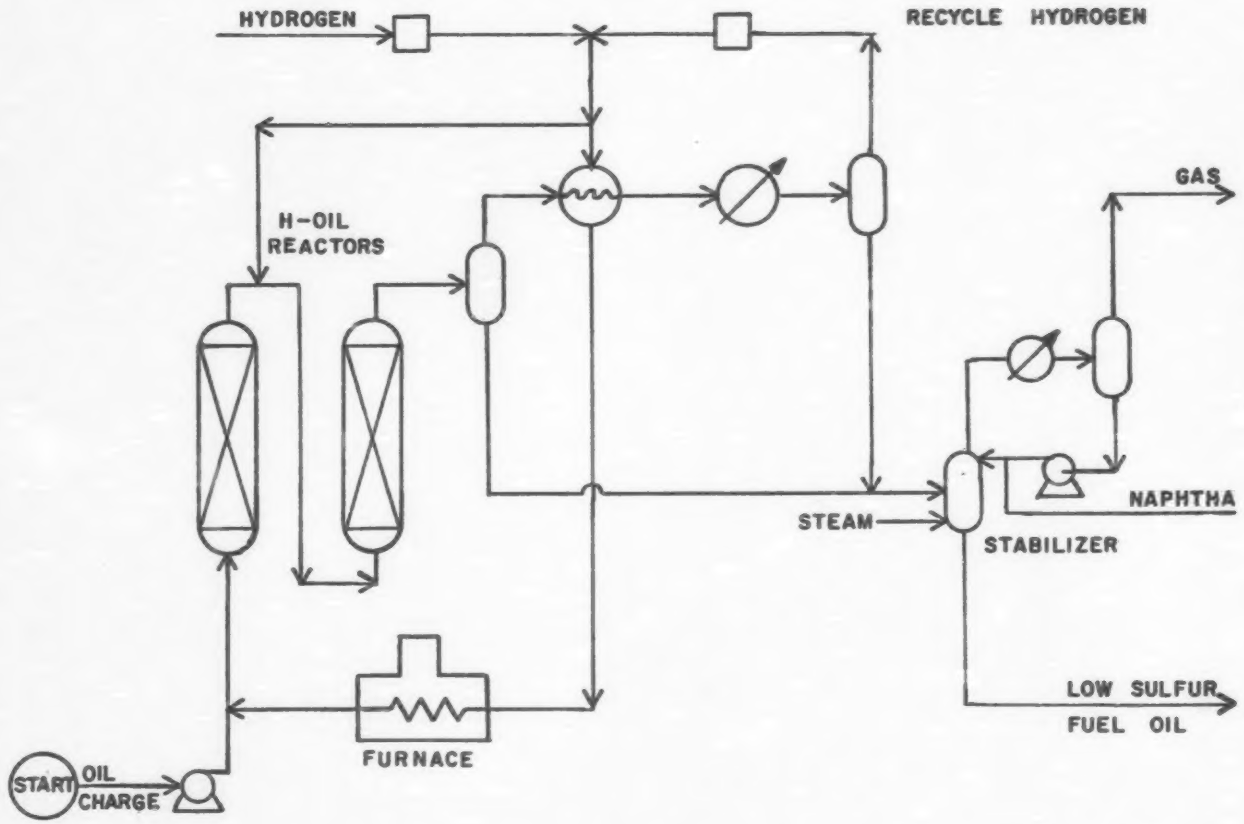

HYDROGEN
RECYCLE HYDROGEN
H-OIL
REACTORS
GAS
NAPHTHA
STEAM
STABILIZER
LOW SULFUR
FUEL OIL
FURNACE
START
OIL
CHARGE

Figure C-7. LC-Fining process flow diagram

Table C-14. DESULFURIZATION OF KUWAIT ATMOSPHERIC BOTTOMS

Objective:	Production of 1.0 wt % sulfur in $650^{\circ}F^{+}$ product
Throughput:	40,000 bpsd (stream factor of 0.9)
Feed inspection:	$650^{\circ}F^{+}$, 15.0 °API, 4.05 wt % S, 49.6 vol % $975^{\circ}F^{+}$

Yields	Wt %	Vol %	°API	Wt % S
(On fresh feed)				
H_2S	3.4	–	–	–
NH_3	0.1	–	–	–
C_1	0.6	–	–	–
C_2	0.6	–	–	–
C_3	0.6	–	–	–
C_4 - 400°F	3.6	4.5	54.0	<0.1
400 - 650°F	23.7	26.6	33.0	0.2
650 - 975°F	38.2	40.8	25.1	0.5
$975^{\circ}F^{+}$	30.2	29.8	13.0	1.7
	101.0	101.7	24.4	0.8
$650^{\circ}F^{+}$	68.4	70.6	19.8	1.0

Hydrogen consumption –	
Chemical	650 scf/bbl
Losses[a]	260 scf/bbl
Total:	910 scf/bbl
Catalyst replacement –	8¢ per barrel of feed oil
Estimated investment[b] –	
Installed cost LC-fining unit	30.0 MM$
Initial catalyst charge	0.6 MM$
Royalty	2.8 MM$
Total:	33.4 MM$
Utilities –	
Power, kW	6,300
Heat @ 75% efficiency, MM Btu/hr	219
Recoverable heat,[c] MM Btu/hr	108
Cooling water @ Δ25°F, gpm	4,590
Labor, operators/shift	3

---

[a] This is with the use of a purge system for purification of recycle gas.

[b] This figure includes major equipment, material, piping, labor, purchasing, engineering, field expenses, a contractor's fee of 6% and 5% for contingencies. Product fractionation is not included. Hydrogen is assumed available at 300 psig and 95 mol % purity. The investment is calculated in U.S. dollars on a 2nd quarter, 1975 basis at a Gulf Coast location.

[c] Enthalpy in reactor liquid stream above 400°F.

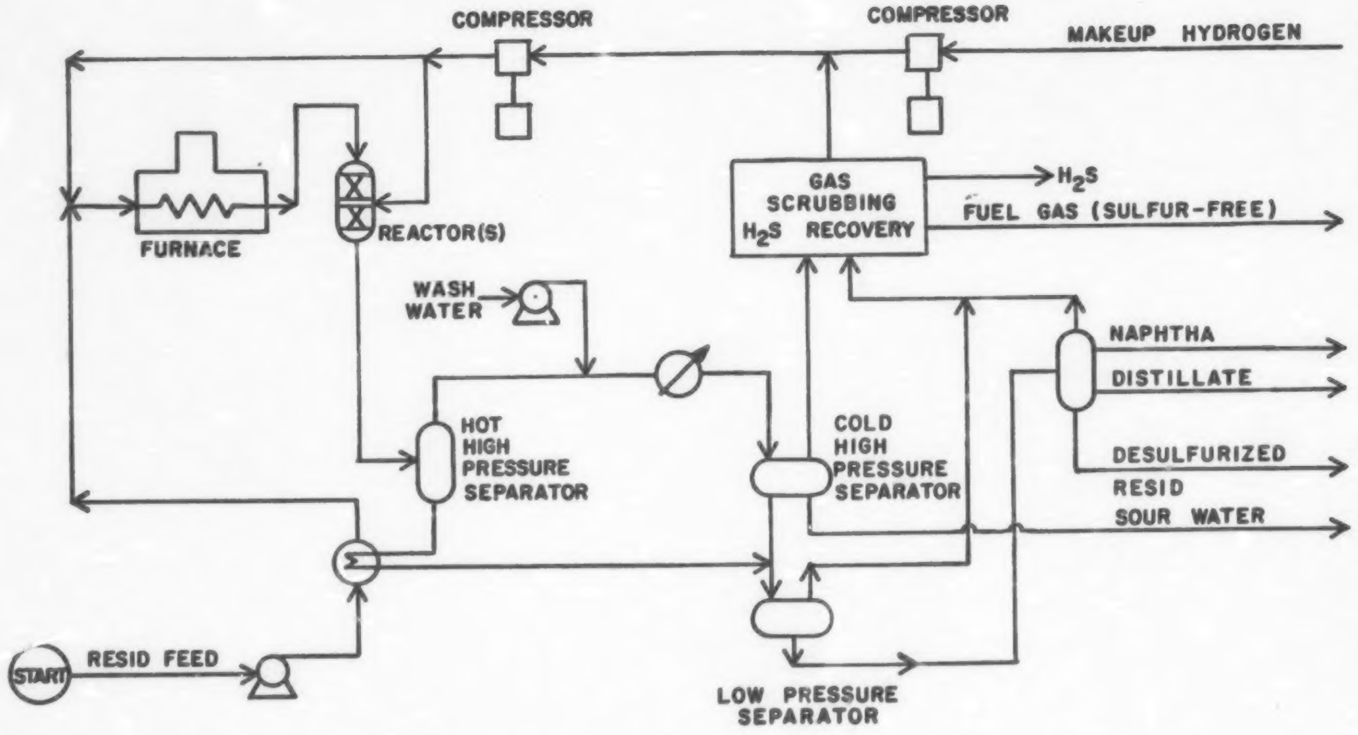

COMPRESSOR
COMPRESSOR
MAKEUP HYDROGEN
GAS SCRUBBING H_2S RECOVERY
H_2S
FUEL GAS (SULFUR-FREE)
FURNACE
REACTOR(S)
WASH WATER
HOT HIGH PRESSURE SEPARATOR
COLD HIGH PRESSURE SEPARATOR
NAPHTHA
DISTILLATE
DESULFURIZED RESID
SOUR WATER
START
RESID FEED
LOW PRESSURE SEPARATOR

Figure C-8. Residual Ultrafining

maintains the temperature and stability of the catalyst. A hot high-pressure separator splits the reactor effluent into a vapor and a bottom stream. The vapors are condensed in an exchanger system leading to a cold high-pressure separator. The hydrogen rich gas is scrubbed with amine to remove hydrogen sulfude and is recycled back to the reactor. Bottoms from the hot high-pressure separator are mixed with the condensed material from the cold high-pressure separator and then flashed in a low-pressure separator. Liquid from this separator is ultimately fractionated into fuel gas, naphtha, distillate and desulfurized resid. The gas streams from the low-pressure separator and the fractionator are scrubbed to produce a sulfur-free fuel gas.

Preliminary data based on bench-scale runs has shown that catalyst life can be expected to last at least 9 months. Deposits of coke as well as nickel and vanadium sulfides have a tendency to shorten catalyst life.

Stage of Development

Numerous resids of widely ranging properties have been desulfurized in both bench-scale and large pilot plant equipment.

Economics

The economics of the Resid Ultrafining process are presented in Tables C-15 and C-16.

GO-FINING (EXXON RESEARCH AND ENGINEERING CO.)[3,20-22]

Go-Fining is a proprietary process for handling high boiling virgin and cracked gas oils. It is a fixed bed system and operates at pressures of 286 to 562 bar (400 to 800 psig).

Table C-15. RESID ULTRAFINING DESULFURIZATION COSTS, BASIS: 40,000 bpsd

Resid	Khafji[a]	West Texas sour[b]	Difference
650+°F product sulfur, wt %	1.0	1.0	—
On-site investment, MM$[c]	17.3	13.0	4.3
Catalyst charge, MM$	1.1	0.4	0.7
Off-site investment, MM$[d]	5.7	4.4	1.3
Total investment, MM$	24.1	17.8	6.3
Cost, ¢/bbl[e]			
Hydrogen	33.5	25.5	8.0
Utilities and chemicals	14.5	13.7	0.8
Catalyst	15.2	5.1	10.1
Labor	1.7	1.7	—
Investment related	41.1	30.5	10.6
Total, ¢/bbl	106.0	76.5	29.5

[a] 78 percent S recovery.

[b] 74 percent S recovery.

[c] Current U.S. Gulf Coast cost (published May 1973) — updated economic data are presented in Appendix D.

[d] Includes working capital.

[e] Per barrel of charge.

Table C-16. WEST TEXAS SOUR DESULFURIZATION COSTS, BASIS: 40,000 bpsd

650+°F product sulfur, wt %	0.3[a]	1.0[b]	Difference
On-site investment, MM$[c]	17.3	13.0	4.3
Catalyst charge, MM$	1.1	0.4	0.7
Off-site investment, MM$[d]	5.7	4.4	1.3
Total investment, MM$	24.1	17.8	6.3
Costs, ¢/bbl[e]			
Hydrogen	34.6	25.5	9.1
Utilities and chemicals	14.5	13.7	0.8
Catalyst	15.2	5.1	10.1
Labor	1.7	1.7	—
Investment related	41.1	30.5	10.6
Total, ¢/bbl	107.1	76.5	30.6

[a] 92 percent S recovery.

[b] 74 percent S recovery.

[c,d,e] See footnotes for Table C-15.

Process Description

Fuel oil and hydrogen rich gas are preheated and fed into a catalytic desulfurization reactor. After being cooled in a heat exchanger, the hydrogen gas is separated from the oil, desulfurized, and either recycled or used in another part of the plant. The desulfurized oil is ultimately stripped of small amounts of low-boiling products and used directly as fuel or stored as a low-sulfur blending stock. Figure C-9 is a schematic of the Go-Fining process.

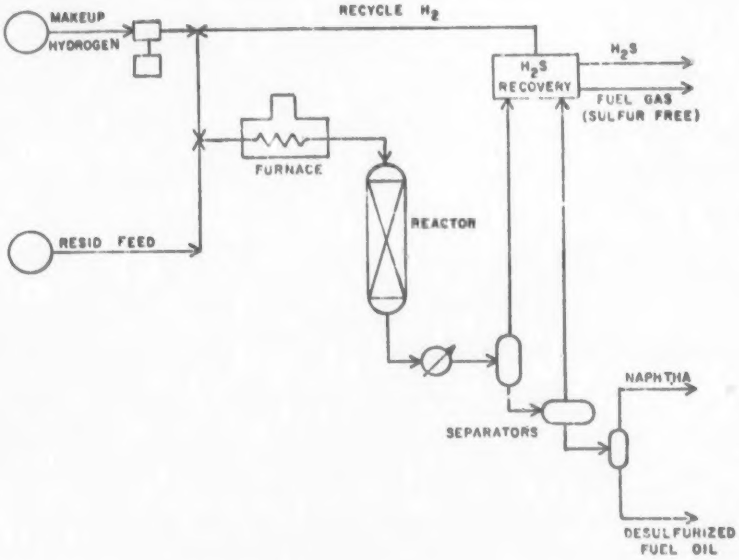

MAKEUP
HYDROGEN
RECYCLE H_2
H_2S RECOVERY
H_2S
FUEL GAS (SULFUR FREE)
FURNACE
REACTOR
RESID FEED
NAPHTHA
SEPARATORS
DESULFURIZED FUEL OIL

Figure C-9. Go-Fining

Depending upon the metals content of the feedstock, the catalyst may be regenerated for longer life and lower operating cost. Typical product yields are presented in Table C-17.

Table C-17. GO-FINING YIELDS AT 90 PERCENT DESULFURIZATION LEVEL (HIGHER LEVELS MAY BE OBTAINED)

Crude source	Kuwait	Arabian light	Khafji	Gach Saran
Feed boiling range, °F	650/1,050°F			
°API	22.2	23.1	21.7	22.4
Sulfur, wt %	3.05	2.28	2.97	1.91
Average yields				
C_4-C_8 (including H_2S), wt %	3.1	2.3	3.1	2.0
C_4 vol %	0.08	0.07	0.09	0.08
C_5–400°F, vol %	0.8	0.6	0.8	0.7
400°F$^+$, vol %	99.0	99.2	99.0	100.0
Sulfur, wt %	0.3	0.23	0.3	0.19
Chemical hydrogen consumption, scf/bbl	280	220	300	220

Economics

Hydrogen consumption ranges from 220 to 300 scf/bbl depending on the amount of sulfur removed and operating pressure. Economic data are presented in Table C-18.

Table C-18. ECONOMICS OF GO-FINING

Economics of go-fining[a]	Per barrel of feed
Investment, $	100-220
Fuel fired, 1,000 Btu	20-40
Power, kW	1-2
Cooling water, gal	200-350
Basis: total erected cost, 1971 Gulf Coast (includes initial charge of catalyst)	

[a] Updated economic data are presented in Appendix D.

Stage of Development

As of September 1972, there were approximately 390,000 bpsd of Go-Fining capacity in units ranging from 15,000 to 80,000 bpsd. An additional total capacity of 580,000 bpsd were in the planning, design, or construction stage.

RESIDFINING (ESSO RESEARCH AND REFINING COMPANY)[3,22,23]

This is a proprietary process for the hydrodesulfurization of atmospheric residue for the production of low sulfur fuel oil.

Process Description

Residfining is a fixed-bed system operating at pressures of approximately 700 bar (1000 psig). The residual oil to be treated and hydrogen-rich gas are preheated before entering the desulfurization reactor. Following heat exchange and cooling, the hydrogen-rich gas is separated from the fuel oil and recycled or used in another process. The desulfurized oil is stripped of small amounts of low-boiling products generated in the reaction and is used directly as fuel or stored for low-sulfur blending stock.

The proprietary catalyst used rejects many of the asphaltenes contained in the residuum. It has been tested using residuum feeds containing 30 to 200 ppm nickel and vanadium with satisfactory results. A schematic is shown in Figure C-10.

Economics

Long catalyst life at low pressure is a significant economic determinant. Operating 700 bar (1000 psig) as opposed to 1400 bar (2000 psig) results in a lower operating cost due to reduced investment, reduced hydrogen consumption, and reduced energy consumption. Economic data are presented in Table C-19.

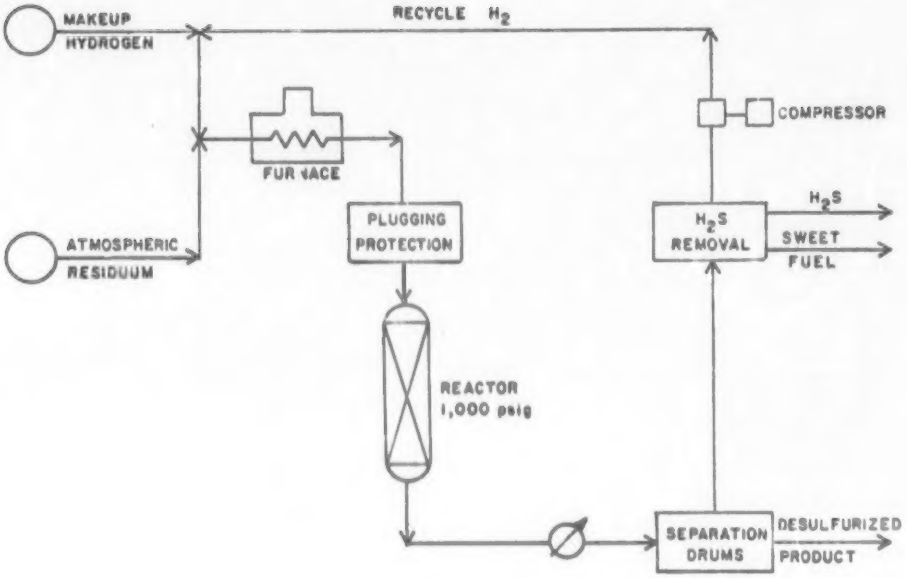

MAKEUP HYDROGEN
RECYCLE H_2
COMPRESSOR
FURNACE
ATMOSPHERIC RESIDUUM
PLUGGING PROTECTION
H_2S REMOVAL
H_2S
SWEET FUEL
REACTOR 1,000 psig
SEPARATION DRUMS
DESULFURIZED PRODUCT

Figure C-10. Schematic of the residfining process

Table C-19. ECONOMICS OF RESIDFINING PROCESS

Economics of residfining[a]	Per barrel of feed
Investment, $[b]	330-500
Power consumption, kW	1.2-1.4
Fuel fired, 1,000 Btu	50-60
Cooling water, gal	200-250

[a] Economic data published September 1972.

[b] Total erected cost: 1971 Gulf Coast; inclusive of catalyst. Updated economic data are presented in Appendix D.

Stage of Development

As of September, 1972, two units were in the design stage.

RESIDUE HYDRODESULFURIZATION[24]

The Badische Anilin-und-Soda-Fabrik AG and Institut Francais du Petrole process is used to remove sulfur, nitrogen and metallic contaminants from heavy feedstocks. Typical charges to the system are atmospheric residue, vacuum residue and total crude oil.

Process Description

A flow diagram of the process is shown in Figure C-11. The feedstock and hydrogen-rich gas plus recycle are preheated in a heat exchanger using the reactor products. The heated charge then enters the fixed bed reactor. After passing through the catalyst bed the reaction products are cooled and sent to separators where the product is desulfurized and separated from the unreacted hydrogen and light hydrocarbons. The product stream is then stabilized in a stripper column.

Three process schemes have been designed to allow for differences in product sulfur content, stream factor and by-product utilization:

- Vacuum gas oil desulfurization - a deep desulfurization of the vacuum gas oil (VGO) and the blending of it with the vacuum residue;
- Indirect desulfurization and solvent deasphalting - the topped crude is distilled, the VGO is deeply desulfurized, the vacuum residue is deasphalted and then desulfurized;
- Direct desulfurization of the topped crude.

See Table C-20 for product yields.

Stage of Development

Not reported.

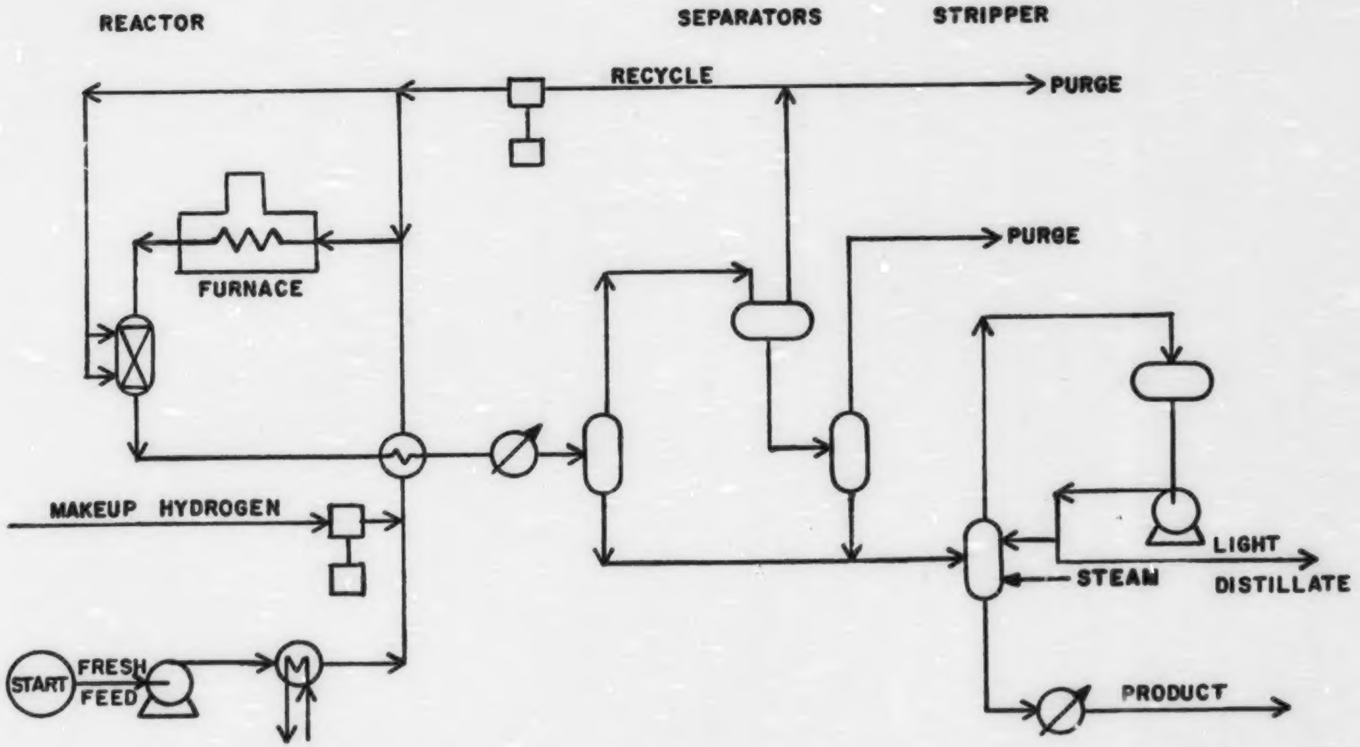

REACTOR
SEPARATORS
STRIPPER
RECYCLE
PURGE
FURNACE
PURGE
MAKEUP HYDROGEN
LIGHT
STEAM
DISTILLATE
START
FRESH
FEED
PRODUCT

Figure C-11. Residue hydrodesulfurization flow diagram

Table C-20. RESIDUE HDS PRODUCT YIELDS

	Ratawi crude	Kuwait crude
Feedstock:		
Specific gravity	0.985	0.969
ASTM distill., IBP, °F	563	574
Sulfur content, wt %	5.1	4.1
Pour point, °F	54	54
Desulfurization rate, %	80	80
Yields (mid-run), wt% on feed:		
$H_2S + NH_3$	4.50	3.60
$C_1 - C_4$	0.80	0.35
C_5 - 302°F	0.60	0.30
302-482°F	2.75	2.50
482 - 662°F	10.50	10.40
662°F	82.50	82.81
Total	101.20	100.96
Product quality:		
Gas-oil, 482 - 662°F		
Specific gravity	0.870	0.867
Sulfur content, wt%	0.065	0.045
Pour point, °F	10.5	10.5
Fuel oil, 662°F$^+$		
Specific gravity	0.941	0.924
Sulfur content, wt%	1.20	0.95
Pour point, °F	54	49

Economics

The economics of the Residue Hydrodesulfurization process are presented in Table C-21.

Table C-21. ECONOMICS OF RESIDUE HDS

A detailed engineering study for a unit treating 45,000 bpsd of Kuwait atmospheric residue at a desulfurization rate of 80 percent gives.[a]	
Investment, $ per bpsd capacity	
Erected battery limits[b]	344
Catalyst, first charge	19
Typical requirement, units per bbl feed	
Electricity, kWh	3.2
Steam (medium pressure), lb	25
Fuel (absorbed heat), M Btu	99
Hydrogen consumption, scf	650
Catalyst life, ultimate, months	12

[a] Economic data published September 1972.

[b] Updated economics data are presented in Appendix D.

HYDRODESULFURIZATION, TRICKLE FLOW[25]

Hydrodesulfurization, Trickle Flow, improves the quality of petroleum fractions ranging from kerosene to heavy gas oil, as well as vacuum flashed distillate by the removal of sulfur and by the hydrogenation of unsaturated components.

Process Description

As shown in Figure C-12, feedstock, combined with hydrogen-rich make-up and recycle gas, is passed through a feed/effluent heat exchanger prior to entering a furnace, where the temperature is raised to 332 to 400°C

(630 to 750°F). The heated charge is then passed through the reactor in a trickle flow. After being cooled the product is flashed in a high-pressure separator at a temperature of 38 to 49°C (100 to 120°F) or for extra heavy gas oils at 149 to 177°C (300 to 350°F). The liquid product is pumped to a work-up section where H_2S and dissolved gases are removed. The gas leaving the high-pressure separator is used as recycle gas. Typical yields from the HDS of thermal cracker gas oil are shown in Table C-22.

Table C-22. TYPICAL RESULTS FROM HYDRODESULFURIZATION OF THERMAL CRACKER GAS OIL (380-650°F FRACTION)

	Feedstock	Product
Specific gravity 20°/4°C	0.8469	0.8326
Sulfur content, wt %	1.33	0.16
Bromine number, g/100 g	23	1
Maleic anhydride value, mg/g	5.2	–
Pour point, °C	-13	-16
Cloud point, °C	-9	-9
Desulfurization, %		88.0
Chemical H_2 consumption, scf/bbl		315
% sulfur removal	88	

Stage of Development

At the end of 1973, 82 units with a combined capacity of 1,050,000 bpsd were operating.

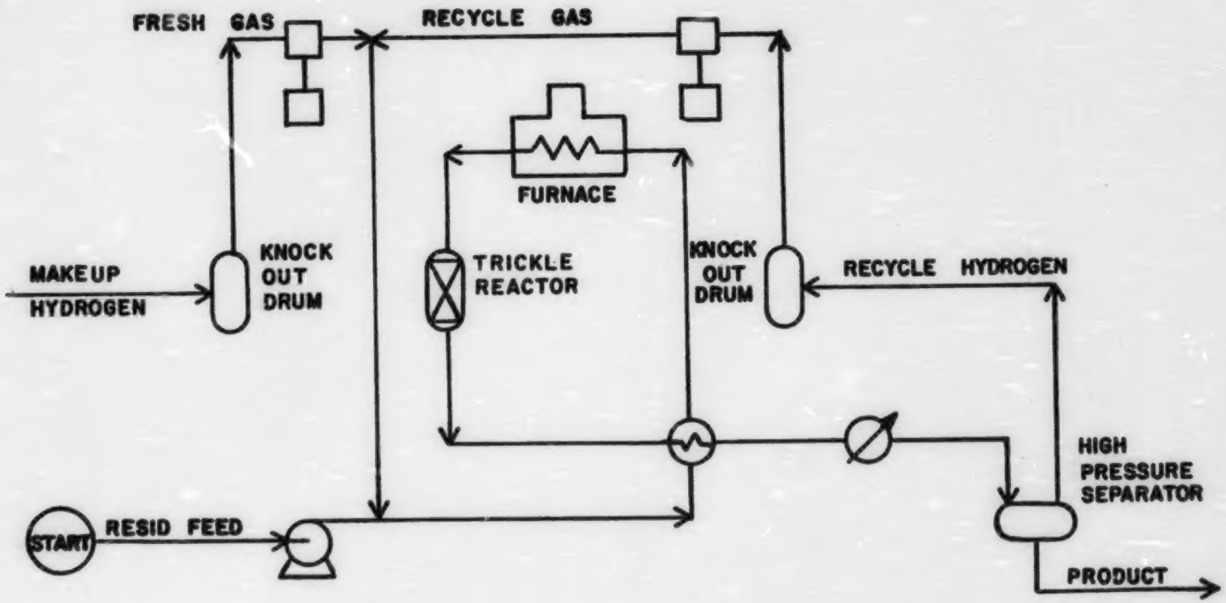

FRESH GAS
RECYCLE GAS
FURNACE
MAKEUP
HYDROGEN
KNOCK
OUT
DRUM
TRICKLE
REACTOR
KNOCK
OUT
DRUM
RECYCLE HYDROGEN
HIGH
PRESSURE
SEPARATOR
START
RESID FEED
PRODUCT

Figure C-12. Hydrodesulfurization, trickle flow, flow diagram

Economics

The economics of the HDS, Trickle Flow, process are described in Table C-23.

Table C-23. ECONOMICS OF HYDRODESULFURIZATION PROCESS

Typical requirement, unit per bbl middle distillate	
Electricity, kwh	1.2
Steam (200 psig), lb	9.6
Fuel, M Btu	52.8
Water, cooling (30°F rise), gal	260
Catalyst consumption, lb	0.01

IFP RESID AND VGO HYDRODESULFURIZATION[3]

The Institut Francais du Petrole's (IFP) HDS process is a catalytic fixed bed operation. This process can be used to improve heavy petroleum stocks by removal of sulfur, nitrogen and metallic contaminants. Typical charges to the reactor are atmospheric residues, vacuum residue and total crude oil. Desulfurization can reach 85 percent.

Process Description

A flow diagram of the IFP hydrodesulfurization process is shown in Figure C-13.

Feed and makeup hydrogen are mixed with a portion of the recycle gas and are then fed down through the catalyst beds. The remaining portion of the recycle gas is used as a temperature regulating quench in the reactor. The reaction products are cooled and sent to a high-pressure separator where hydrogen-rich gas is removed and recycled to the reactor. The product is stabilized in a stripper column where light ends and residual H_2S are removed.

In this process, IFP employs a cobalt molybdate catalyst in the form of extrudates 1.5 mm in diameter and 3 to 6 mm long.

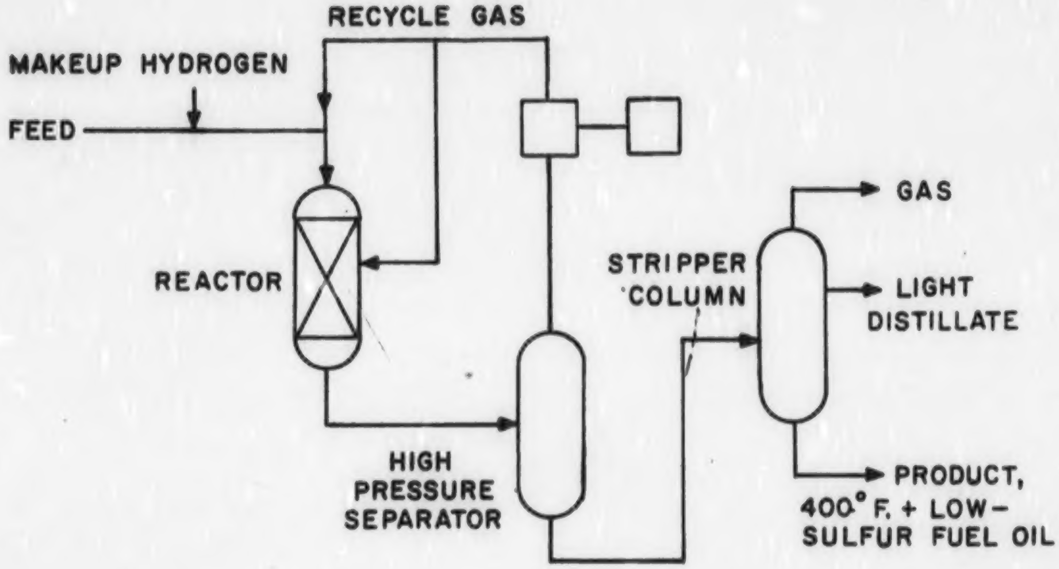

RECYCLE GAS
MAKEUP HYDROGEN
FEED
REACTOR
HIGH PRESSURE SEPARATOR
STRIPPER COLUMN
GAS
LIGHT DISTILLATE
PRODUCT, 400° F. + LOW-SULFUR FUEL OIL

Figure C-13. IFP resid and VGO desulfurization flow diagram

Tables C-24 and C-25 give feed and product specifications for a Kuwait residue.

Table C-24. FEED SPECS AND IFP PROCESS PERFORMANCE

Kuwait residue	
Gravity	15.5° API
Sulfur	4.1 wt %
Nitrogen	2,500 wt ppm
Metals	63 wt ppm
Conradson carbon	9.5 wt %
Asphaltenes	2.6 wt %
Viscosity at 210°F	160 SUS
Pour point	52°F.
ASTM distribution IBP	572°F.
5%	716°F.
50%	1,013°F.
Desulfurization rate	89%
Hydrogen chemical consumption	760 scf/bbl
Catalyst ultimate life	9 months

Table C-25. YIELDS FROM KUWAIT RESIDUE

Yields, mid run	
$H_2S + NH_3$	3.85 wt% on feed
C_1-C_4	0.55 wt% on feed
C_5-400°F	3.0 wt% on feed
400°F+	93.8 wt% on feed
	(=99.50 vol% on feed
Long residue 400°F+	
Gravity	24.8
Sulfur	0.50 wt%
Flash point	300°F.
Metals	17 ppm
Viscosity at 210°F	80 SSU
Asphaltenes	0.6 wt%

Stage of Development

As of September 1972 two plants were in operation, one in Japan and the other in the Near East.

Economics

The economics of the IFP HDS process are presented below in Table C-26.

Table C-26. TYPICAL ECONOMICS OF IFP HDS PROCESS (WITH IRANIAN LIGHT ATMOSPHERIC RESIDUE)[a]

Charge:	$650^{\circ}F$ IBP 25 API 2.5 wt % S	
Plant capacity:	40,000 b/sd	
$400^{\circ}F^{+}$ cut:	0.3 wt % S 99 vol % yield on feed	
Investment:	$20,000,000	
¢/bbl feed:	Cost	Credit
Hydrogen[b]	24.0	
Catalyst	11.0	
Utilities[c]	5.5	
Investment related[d]	31.4	
Sulfur[e]		4.4
Totals	71.9	4.4
Net charges: 67.5 ¢/bbl of feed 68.2 ¢/bbl of fuel $400^{\circ}F^{+}$		

[a] As of September 1972 updated economic data are presented in Appendix D.

[b] 35¢/Mscf.

[c] Power 1¢/kW, fuel 25¢/MM Btu, steam 0.08¢/lb. Light products counted for fuel.

[d] 20 percent/year of investment cost including amortization, interest, maintenance, labor and overhead (includes amine washing, sulfur plant and gas cleaning).

[e] $15/long ton.

DEMETALIZATION/DESULFURIZATION[26]

As the metals content (principally vanadium) increases in residual feedstock, the cost of desulfurizing increases due to larger reactor volumes and higher catalyst usage. When processing residual fuel oils with vanadium contents above 200 to 300 ppm, the economics may favor a scheme of demetallization/desulfurization.

Process Description

This method uses a recently developed system employing two different catalysts (see Figure C-14). The first catalyst system uses a demetallization ebullating bed reactor containing an inexpensive natural catalyst. This reactor is followed by one or more desulfurization ebullating bed reactors containing a conventional Co-Mo catalyst. The demetallization and desulfurization reactor designs are similar. The advantage of this technique lies with the natural catalyst used for demetallization, the cost of which is about 5 to 10 percent of the Co-Mo catalyst.

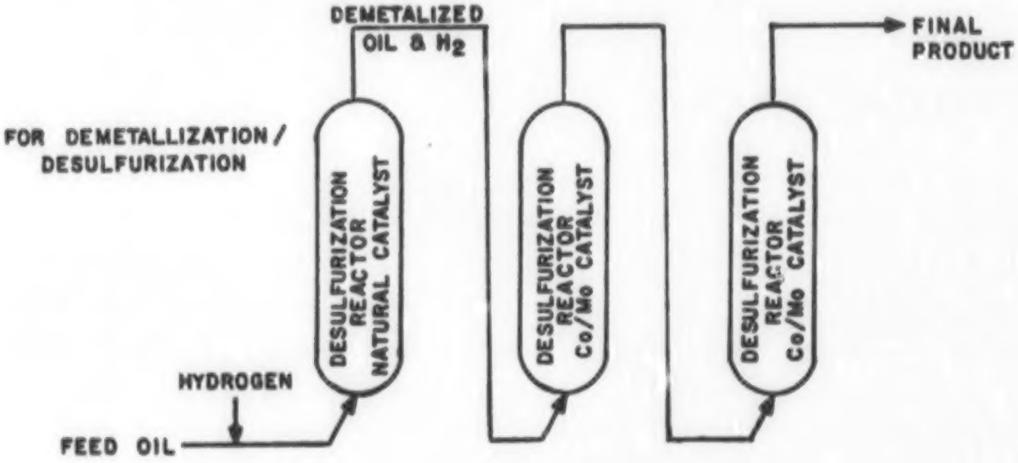

DEMETALIZED OIL & H_2
FINAL PRODUCT
FOR DEMETALLIZATION / DESULFURIZATION
DESULFURIZATION REACTOR NATURAL CATALYST
DESULFURIZATION REACTOR Co/Mo CATALYST
DESULFURIZATION REACTOR Co/Mo CATALYST
HYDROGEN
FEED OIL

Figure C-14. Demetalization/desulfurization flow diagram

Stage of Development

Several pilot plant studies have been performed successfully using medium-metals-content (400 ppm vanadium) atmospheric bottoms and Boscan high metals crude (1100 ppm vanadium).

Economics

The economics of the demetalization/desulfurization system are presented in Table C-27.

DELAYED COKING[23,27]

The process of Delayed Coking upgrades heavy residuals or bottom of the barrel materials into more valuable distillate products and coke. By 1980 the production of coke is expected to exceed 4.5 x 10^7 kg (50,000 tons) per day. Delayed coking accepts as feed material a full range of reduced crude oils, shale oil, Athabasca bitumen, gilsonite, coal tar pitch, and asphalt. Needle coke for electrodes in aluminum manufacture is produced as a side product from aromatic and refractory stocks, such as catalytic cycle oils and thermal tars.

Process Description

A flow diagram of a simplified delayed coking and fractionation section is shown in Figure C-15. The feed material is fed directly to the bottom section of the fractionator where material lighter than the desired end point of the heavy gas oil is flashed off. The remaining material from the bottom of the fractionator is combined with recycle oil and is pumped to the coking heater where it is rapidly heated to above 482°C (900°F). The liquid-vapor mixture then leaves the coking heater and enters a coke drum.

Table C-27. COST COMPARISON[a] – DESULFURIZATION VERSUS DEMETALIZATION/DESULFURIZATION

	Venezuelan medium-metals atmospheric residuum		Venezuelan high-metals crude, Boscan	
Throughput, b/sd	25,000	25,000	25,000	25,000
Type operation	Desulfurization	Demetallization/ desulfurization	Desulfurization	Demetallization/ desulfurization
Feedstock data				
Gravity, °API	11.8	12.7	10.4	10.4
V, ppm	375	398	1,100	1,100
Space velocity				
Vo/hr/Vr (Case 1 = 1.00)	0.49	0.31	0.53	0.49
Hydrogen cons., scf/bbl	720	680	1,140	1,030
Investment, \$ million[b]	19.8	25.2	21.8	23.9
Major processing cost				
Catalyst cost, ¢/bbl	42	13	62	11
Hydrogen, ¢/bbl[c]	54	51	86	77
Investment, ¢/bbl[d]	24	31	26	29
Total, ¢/bbl	120	95	174	117

[a] Article published June 1975, updated economic data are presented in Appendix D.

[b] Investment includes demetallization (if any)/desulfurization sections at a Gulf Coast location.

[c] Hydrogen is assumed to be from steam-methane reforming at 75¢/1.000 scf.

[d] Investment payout over 10 years in ¢/bbl based on 0.90 on-stream factor.

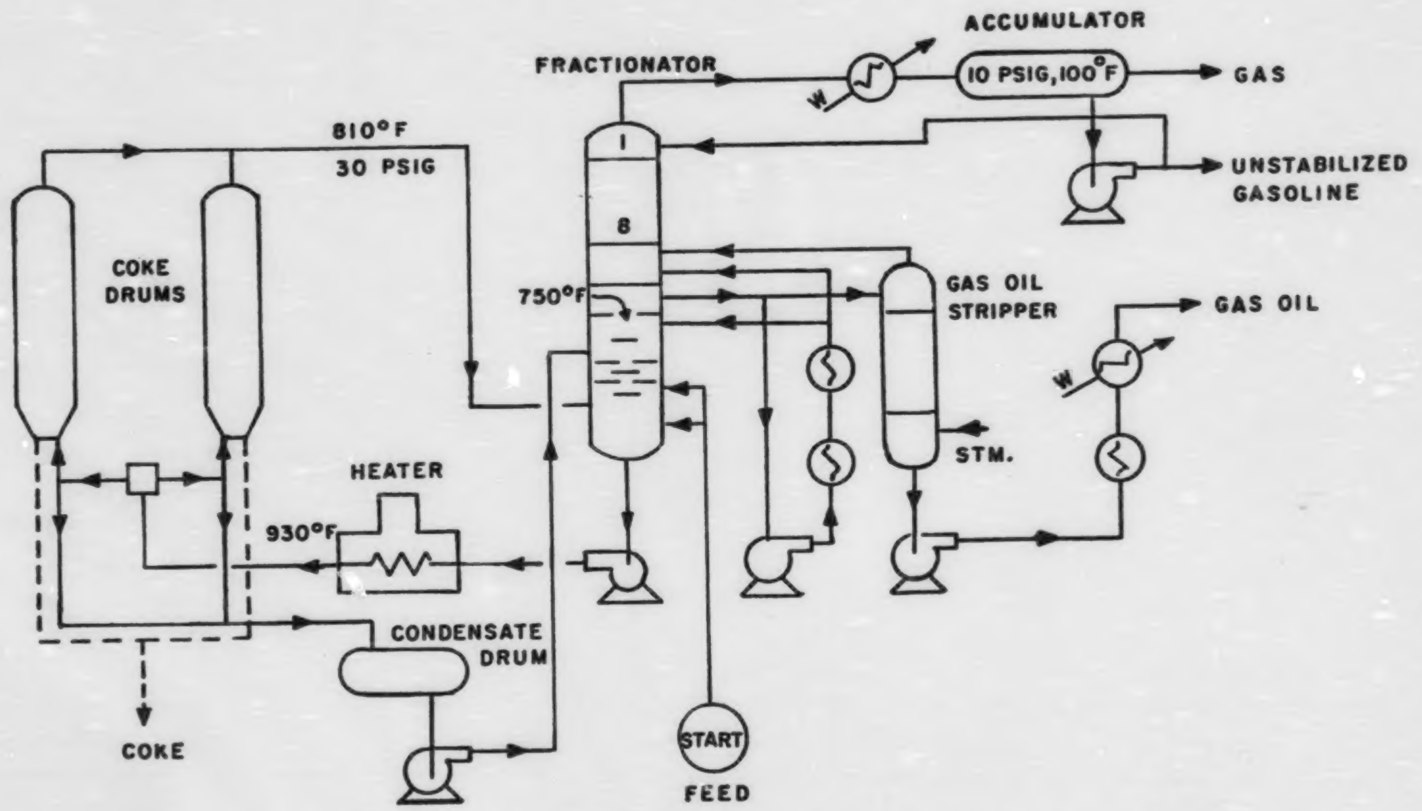

ACCUMULATOR
FRACTIONATOR
10 PSIG,100°F
GAS
810°F
30 PSIG
UNSTABILIZED GASOLINE
1
8
COKE DRUMS
750°F
GAS OIL STRIPPER
GAS OIL
W
W
STM.
HEATER
930°F
CONDENSATE DRUM
COKE
START
FEED

Figure C-15. Simplified flow diagram for delayed coking

A coking unit usually has two drums, one on stream while the other is being decoked. The coke units are usually designed so that each one operates on a 48-hour cycle. The overhead vapors from the coke drum enter the lower section of the fractionating tower for separation into gas, gasoline, gas oils and recycle stock.

Stage of Development

Delayed Coking has been used extensively in the petroleum industry for several years. Coking capacity by the end of the seventies is expected to grow to between 4.1×10^7 and 4.5×10^7 kg (45,000 and 50,000 tons) per day. As advancements in operating techniques are made, a wider range of feed stocks will be utilized. Several units are currently operating successfully outside the U.S. and are designed for a coal tar pitch feed.

Economics

No data available.

VGO/VRDS ISOMAX[12,28,29]

The combination of a vacuum gas oil desulfurizer (VGO Isomax) with a vacuum residuum desulfurizer (VRDS Isomax) is often an attractive alternative to direct desulfurization of atmospheric residuum (RDS Isomax). The VGO/VRDS is an extension of RDS technology; the major difference involving feed stock and type of catalyst.

Process Description

The separation of atmospheric residuum into a gas-oil fraction and a vacuum-tower bottom combined with desulfurization of each stream individually requires 35 percent less hydrogen than direct desulfurization of atmospheric residuum as is the case in the RDS process. In addition, the yield of heavy fuel oil (659°F$^+$) is 2 to 3 percent higher in the VGO/VRDS combination process.

Vacuum gas oil is processed at considerably lower pressures than the residue, which leads to a very selective hydrodesulfurization with minimum hydrogen-consuming side reactions. Table C-28 shows the yields from Arabian light residuum using VGO, VRDS and RDS processes. As indicated in this table, the VGO process produces 0.1 percent sulfur product which when combined with the VRDS product yields an overall 0.5 percent sulfur fuel oil. Figure C-16 presents a flow diagram of a VGO/VRDS process.

Table C-28. LOW SULFUR FUEL OIL PRODUCTION FROM ARABIAN LIGHT RESIDUUM[a]

Process	VGO	VRDS	VGO+ VRDS	RDS
Feed sulfur, wt %	2.3	4.1	2.9	2.9
Product sulfur, wt %	0.[illegible]	1.28	0.5	0.5
Product yields				
C_1-C_4, wt %	0.59	0.56	0.58	0.58
H_2S, NH_3, wt %	2.44	3.00	2.55	2.55
C_5^+, wt %	97.51	97.34	97.46	97.67
C_5^+, LV %	100.6	102.0	101.0	101.5
Hydrogen consumption				
Scf/bbl	330	720	450	550
Scf/lb sulfur	47	71	56	69

[a] Chevron hydrotreating process yields (middle of run).

Stage of Development

The development status of VGO Isomax plants is presented in Table C-29.

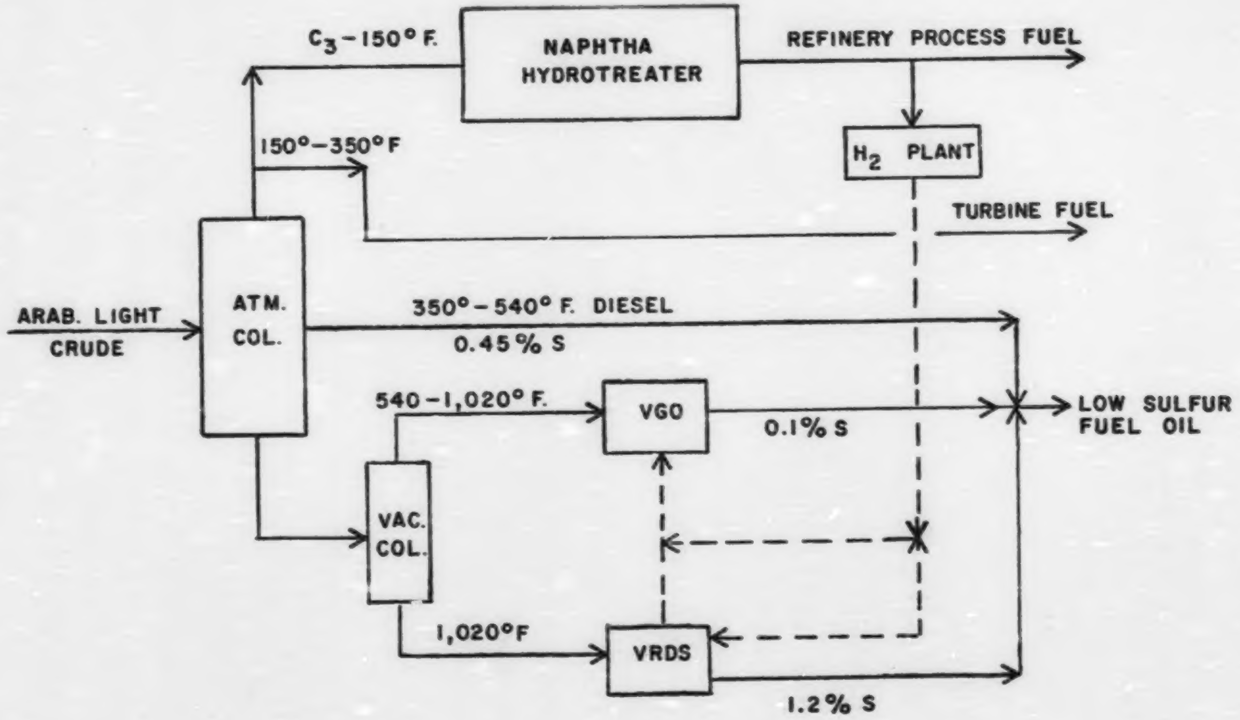

C3 - 150° F.
NAPHTHA HYDROTREATER
REFINERY PROCESS FUEL
H2 PLANT
150°-350°F
TURBINE FUEL
ARAB. LIGHT CRUDE
ATM. COL.
350° - 540° F. DIESEL
0.45% S
540-1,020° F.
VGO
0.1% S
LOW SULFUR FUEL OIL
VAC. COL.
1,020°F
VRDS
1.2% S

Figure C-16. VGO/VRDS flow diagram

Table C-29. VGO ISOMAX PLANTS[a]

Company	Location	Capacity, b/sd
On-stream		
Chevron Oil Co.	Salt Lake City, Utah	5,200
Fuji Oil Co.	Sodeguara, Japan	23,000
Koa Oil Co.	Marifu, Japan	8,000
Koa Oil Co.	Osaka, Japan	12,000
Nippon Petroleum Refining Co.	Negishi, Japan	40,000
Subtotal		88,200
Engineering and construction		
Asia Kyoseki Co.	Sakaide, Japan	15,000
Nippon Petroleum Refining Co.	Negishi, Japan	28,000
Nippon Petroleum Refining Co.	Muroran, Japan	40,000
Tohoku Oil Co.	Sendai, Japan	35,000
Bahrain Petroleum Co.	Bahrain, Arabian Gulf	50,000
Kashima Oil Co.	Kashima, Japan	25,000
Unannounced		60,000
Unannounced		36,000
Subtotal		289,000
Total		377,200

[a] As of September 1972.

Economics

Tables C-30 and C-31 present the differences in investment and processing costs for a VGO/VRDS process and a RDS process.

Table C-30. INVESTMENT SUMMARY

Feed: 86,000 b/cd Arabian light $650^{o}F^{+}$ residuum

Product: $350^{o}F^{+}$ fuel oil containing 0.5 % sulfur

Processing scheme On-plot investment,[a] $ millions, relative to RDS -	VGO/VRDS
Crude unit	+ 7
H2 plant	- 3
VGO, VRDS	-11
Total	- 7

[a] U.S. Gulf Coast estimates for January 1975. List does not include the process equipment common to both cases.

Table C-31. PROCESSING COSTS

Feed: 86,000 b/cd Arabian light $650^{o}F^{+}$ residuum

Product: $350^{o}F^{+}$ fuel oil containing 0.5 % sulfur

Processing scheme	VGO/VRDS
Amortization, $/bbl F.O. relative to RDS	-0.05
Operating costs, $/bbl F.O.[b] relative to RDS	
Catalyst	0
Hydrogen	-0.20
Utilities	-0.04
Other	+0.09
Total	-0.20

[a] Includes only on-plot investment for crude unit, hydrogen plant, and hydrotreaters.

[b] Utility costs are: fuel $13/bbl equivalent fuel oil; steam $2/1,000 lb; cooling water and process water $0.26/1,000 gal; power $0.027/kWh.

SHELL GASIFICATION PROCESS[30,31]

The Shell Gasification Process (SGP) in conjunction with a combined cycle is based on a new application of SGP developed in the Amsterdam research laboratories of Royal Dutch Shell during the early 1950's.

Process Description

The SGP involves the partial combustion of heavy, sulfur-containing residual fuels and heavy crude oils to produce a mixture of hydrogen and carbon monoxide. Hydrogen sulfide produced during this reaction is readily removed to yield a sulfur-free (5 ppm) fuel gas, which is used for power generation in a typical combined cycle. Figure C-17 contains a schematic diagram of this SGP/combined cycle process.

A simplified SGP flow diagram is shown in Figure C-18. The hydrocarbon charge and the oxidant are preheated and fed to the reactor. Hot reactor-effluent gas, containing about 3 percent of the feed as soot, is passed to a waste-heat boiler, producing high-pressure saturated steam. High heat-transfer rates assure that the temperature of the gas leaving the waste-heat boiler is close to that of the steam produced in the boiler.

The design and construction of the waste-heat boiler are such that the surface remains clean for an indefinite period (without using external cleaning devices). The waste-heat boiler of the Shell prototype unit has been in operation since 1956 and never has been cleaned on the gas side. This waste-heat boiler can be designed for steam pressure up to about 1 kbar (1,500 psig).

Gas Cleanup

The "crude" gas leaving the waste-heat boiler at temperatures around 177°C (350°F) is then passed to the carbon-removal system. In this system

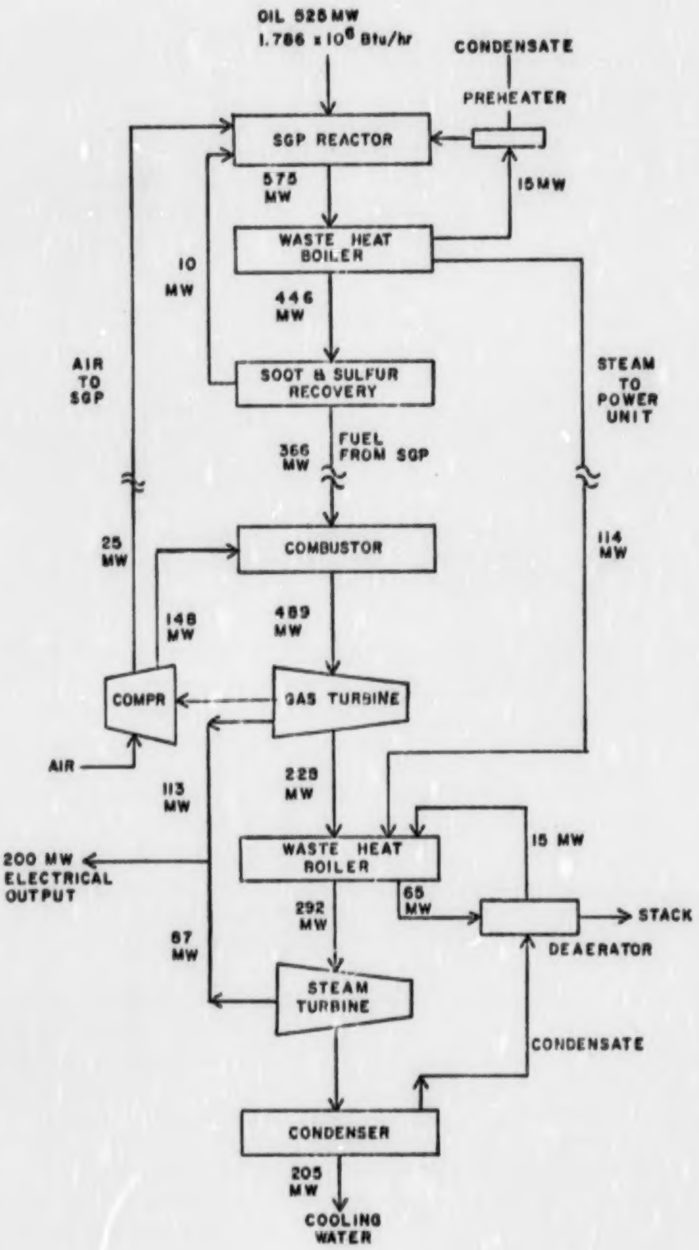

OIL 525 MW
1.786 x 10^6 Btu/hr
CONDENSATE
PREHEATER
SGP REACTOR
575 MW
15 MW
WASTE HEAT BOILER
10 MW
446 MW
AIR TO SGP
SOOT & SULFUR RECOVERY
STEAM TO POWER UNIT
366 MW
FUEL FROM SGP
25 MW
COMBUSTOR
114 MW
148 MW
489 MW
COMPR
GAS TURBINE
AIR
113 MW
228 MW
WASTE HEAT BOILER
15 MW
200 MW ELECTRICAL OUTPUT
292 MW
65 MW
STACK
DEAERATOR
87 MW
STEAM TURBINE
CONDENSATE
CONDENSER
205 MW
COOLING WATER

Figure C-17. Combined cycle/shell gasification process

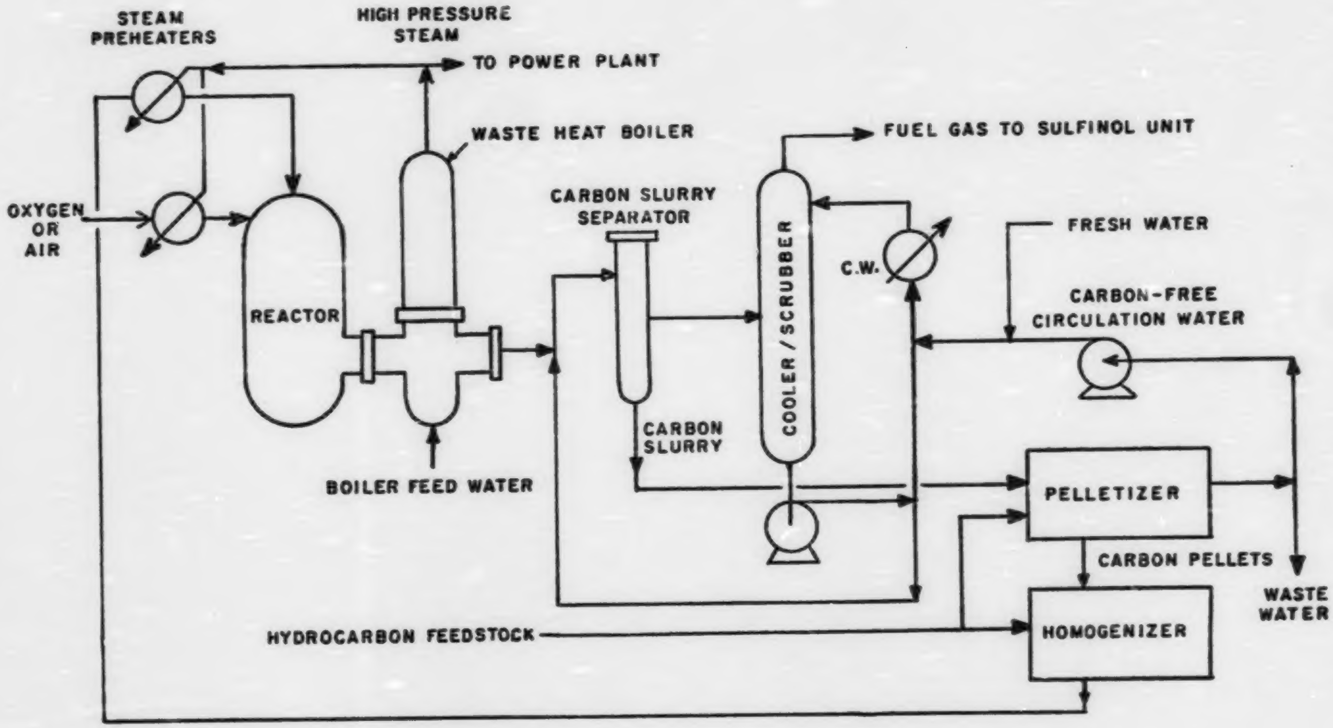

STEAM PREHEATERS
HIGH PRESSURE STEAM
TO POWER PLANT
WASTE HEAT BOILER
FUEL GAS TO SULFINOL UNIT
OXYGEN OR AIR
CARBON SLURRY SEPARATOR
COOLER / SCRUBBER
C.W.
FRESH WATER
CARBON-FREE CIRCULATION WATER
REACTOR
CARBON SLURRY
BOILER FEED WATER
PELLETIZER
CARBON PELLETS
WASTE WATER
HYDROCARBON FEEDSTOCK
HOMOGENIZER

Figure C-18. Shell gasification power generation block diagram bulk removal of the carbon is accomplished by contact of the gas with water. The remaining product gas has less than 5 ppm of carbon. The carbon produced in the gasification is recovered as a soot in a water slurry (carbon content 1 percent to 2 percent by weight). In most cases, it would not be possible to dispose of this untreated carbon slurry. Therefore, Shell has developed a technique for removing carbon from the slurry permitting the water to be reused. Depending on the metals content of the feedstock and the economics and maintenance policy of the process operator, Shell claims that up to 100 percent of the soot can be recycled to extinction with the fresh feed.

Sulfur in the feedstock is converted primarily to H_2S and traces of COS. The carbon-free product gas is treated in a Shell Sulfinol or ADIP process unit, where the sulfur compounds and most of the CO_2 are absorbed. The desulfurized gas is said to contain typically less than 5 ppm of sulfur. The acid-gas effluent from the Sulfinol unit is fed to a Claus process unit, which recovers elemental, salable sulfur.

Either oxygen or air can be used as the oxidant depending on the desired heating value in the product gas. Nitrogen present in the air will act as a moderator for temperature control in the reactor. In either case, steam is injected into the reactor for further temperature control. Air oxidation produces a low-heating-value 1068 $kcal/m^3$ (120 Btu/ft^3) fuel gas, while oxygen feed produces a medium-heating-value gas 2670 $kcal/m^3$ (300 Btu/ft^3). Typical product-gas compositions for air and oxygen gasification are shown in Table C-32.

Table C-32. TYPICAL PRODUCT GAS COMPOSITION

	% vol, dry basis	
	O_2 oxidation	Air oxidation
Hydrogen	48.0	12.0
Carbon monoxide	51.0	21.0
Methane	0.6	0.6
Nitrogen	0.2	66.0
Argon	0.2	0.4
Sulfur	5 ppm	5 ppm
Total	100.0	100.0

Economics

The economics of the Shell gasification process are presented in Table C-33.

Table C-33. POWER GENERATION COST - 200-MW STUDY[a]

Gross output, Mw[b]	200.0
Power consumed, Mw	4.7
Net power output, Mw	195.3
Overall efficiency, %	38.0
Capital cost, $ millions (1972)	
Fuel-processing unit	18.2
Power-generation unit	31.4
Total capital cost	49.6
Operating cost, mills/kwhr	
Sulfur credit @ $10/ton	(0.06)
Catalysts and chemicals	0.06
Water costs	0.40
Operating labor @ $83,500/job (4 operators)	0.20
Maintenance @ 3% of capital	0.85
Local overhead @ 100% labor plus 25% maintenance	0.41
Taxes and insurance @ 1% of capital	0.29
Total net operating cost	2.15
Fuel cost (X = dollar cost per bbl of oil)	1.52X

[a] Yearly average value. Actual capacity is 11% higher to compensate for 90% stream factor.

[b] Cost data published February 1973. Basis 10,000 bpsd; updated economic data are presented in Appendix D.

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APPENDIX D

ECONOMICS AND PROCESS PARAMETERS OF ALTERNATIVE RESIDUAL OIL UTILIZATION TECHNOLOGIES

INTRODUCTION

This section summarizes the technical details and economics of the systems presented in the preceding two appendices. The concluding portion of this section compares the costs of the CAFB with the costs of feedstock desulfurization and flue gas desulfurization.

PROCESS PARAMETERS OF FEEDSTOCK DESULFURIZATION

Table D-1 summarizes the feed types, desulfurization efficiencies and hydrogen and water requirements of the three feedstock desulfurization techniques capable of handling high metal feedstock. Table D-2 presents the same data for the other processes described in Appendix C.

ECONOMICS OF FEEDSTOCK DESULFURIZATION PROCESSES

Cost data presented in Appendix C are taken directly from literature published by system developers. It is difficult to accurately compare process costs for the following reasons:

- Differences in feedstock
    - Source
    - Sulfur content
    - Metals content

Table D-1. PROCESS PARAMETERS OF HIGH METALS FEEDSTOCK DESULFURIZATION TECHNIQUES

Process	Feed type	% S feed	% S product	% S removal	Metals feed, ppm	Metals product, ppm	H_2 consumption, scf/bbl	Water usage
Flexicoking	Iranium heavy	3.43	0.2 equiv.	94% equiv.	525	5	-	20-30 gal/bbl cooling 12-16 gal/bbl boiler feed
	Bachaquero	3.66	0.2 equiv.	95% equiv.	1040	10	-	20-30 gal/bbl cooling 12-16 gal/bbl boiler feed
	W. Texas	4.6	0.2 equiv.	96% equiv.	137	1	-	20-30 gal/bbl cooling 12-16 gal/bbl boiler feed
Demetalization/ Desulfurization	Venezuelan high metals crude	5.6	1.27	77	Ni - 85 V - 1100		1140	-
	Venezuelan medium metals atm resid	2.8	0.64	77	Ni - 57 V - 398		680	-
L. C. Fining	Kuwait	4.05	1.0	75	Ni - 15 V - 49	-	910	4590 gal/min Δ25°F cooling
	atm resid	4.05	0.5	88	Ni - 15 V - 49	-	1030	4860 gal/min Δ25°F cooling
	Gach Saran	2.6	1.0	62	Ni - 45 V - 165	-	540	5410 gal/min Δ25°F cooling
	atm resid	2.6	0.5	81	Ni - 45 V - 165	-	630	5830 gal/min Δ25°F cooling

Table D-2. PROCESS PARAMETERS OF RESIDUAL OIL FEEDSTOCK DESULFURIZATION TECHNIQUES

Process	Feed type	% S feed	% S product	% S removal	Metals feed, ppm	Metals product, ppm	H_2 consumption, scf/bbl	Water usage
HDS-Gulf	Kuwait	3.8	1.0	75	60	0.2	515	214 gal/bbl cooling Δ20°F
		3.8	0.3	92	60	<0.1	740	288 gal/bbl cooling Δ20°F
		3.8	0.1	97	60	<0.1	900	355 gal/bbl cooling Δ20°F
RCD Isomax	Kuwait	3.92	1.0	74	Ni - 15 V - 47	- -	600	-
Universal Oil Products Co.		4.1	0.3	93	Ni - 15 V - 47	- -	750	-
	Direct I	3.9	1.0	74	Ni - 15 V - 45	- -	550	-
	Direct II	3.9	0.5	87	Ni - 15 V - 45	- -	770	-
	Modified Direct III	3.9	0.32	92	Ni - 15 V - 45	- -	850	-
Residue Desulfurization BP	Kuwait	4.0	1.0	75	Ni - 13 V - 49	Ni - 6 V - 18	625	-
		4.0	0.5	88	Ni - 13 V - 49	Ni - 4 V - 13	835	-
		4.0	0.3	93	Ni - 13 V - 49	Ni - 3 V - 12	1050	-
Residue Hydroprocessing	Kuwait	4.02	1.0	75	69	16	560-620	160 gal/bbl cooling 4.2 gal/bbl process
Standard Oil Co.		4.02	0.5	88	69	5	560-620	160 gal/bbl cooling 4.2 gal/bbl process
Residue Ultrafining	Khafyi	4.47	1.0	78	Ni - 93 V - 32	-	580	-
Amoco	W. Texas Sour	3.85	1.0	74	Ni - 25 V - 16		420	-
		3.85	0.3	92	Ni - 25 V - 16		600	-

Table D-2 (continued). PROCESS PHYSICAL PARAMETERS OF RESIDUAL OIL FEEDSTOCK DESULFURIZATION TECHNIQUES

Process	Feed type	% S feed	% S product	% S removal	Metals feed, ppm	Metals product, ppm	H_2 consumption, scf/bbl	Water usage
Go-fining	Arab Heavy	2.96	0.1	97	-	-	410	30-50 gal/bbl cooling
Exxon	Athabasca sands	3.97	0.11	97	-	-	975	30-50 gal/bbl cooling
Resid fining	Gach Saran	2.5	0.3	88	220	-	625	150-300 gal/bbl cooling
Exxon	Arab Heavy	4.19	0.3	93	120	-	915	150-300 gal/bbl cooling
Residue HDS	Kuwait	4.1	0.95	77	-	-	650	-
Badische Anilin-und Soda-Fabrik A.G.								
HDS - Trickle Flow	Thermal cracker gas	1.33	0.16	88	-	-		260 gal/bbl cooling Δ30°F
IFP Residue and VGO HDS	Iranian Light	2.5	0.3	88			232	37.7 gal/bbl cooling
Institute Francais du Petrole	Atmospheirc							

- Differences in amortization rates
- Differences in assumed costs of hydrogen and other materials
  - For example, the reported price of hydrogen varies between 25¢ and $1.00 per thousand standard cubic feet of gas
- Differences in plant sizes
- Unpublished assumptions regarding labor costs, transportation costs, etc.

With these caveats in mind Table D-3 is presented to summarize the economics of the processes described in Appendix C. The column labeled "GCA estimated operating costs" represents an attempt to report process costs on a common basis in 1975 dollars. The figures in this column were calculated based upon estimated operating costs of 75¢ per thousand SCF of H_2 and 15 percent investment related costs.

It is difficult to put the capital costs in Table D-3 on the same basis. However, the investment related costs always include process equipment costs and may or may not include direct labor costs or fee. Therefore, when comparing costs in Table D-3, process descriptions in Appendix C should be consulted to insure that capital costs are calculated on the same basis.

ECONOMIC COMPARISON OF FGD, HDS AND CAFB

Westinghouse has generated both operating and capital costs for a limestone scrubbing FGD unit[32] based on a previous comprehensive study of FGD economics prepared by EPA/TVA.[33] Westinghouse has also generated the HDS operating and capital costs on the same basis as the FGD costs. The capital costs for FGD and HDS are given in Table D-4 for two different size plants. Foster-Wheeler projects a cost of $23,975,905 for their 250 Mw oil gasifier including engineering and fee. As can be seen from Table D-4, FGD presents the smallest capital cost while CAFB and HDS are roughly equivalent.

Table D-3. ECONOMICS FOR OTHER RESIDUAL OIL UTILIZATION TECHNIQUES

Process	Feed type	Cost basis, bpsd	% S feed	% S product	% S removal	Investment		Operating cost		GCA estimated operating cost, $/bbl	References
						Total MM, $	Per bbl, capacity, $	Total MM, $	Per bbl, capacity, $		
HDS-Gulf	Kuwait Type II	50,000	3.8	1.0	74		1.58		-	0.85	1, 2, 3, 4, 5
	Type III	50,000	3.8	0.3	92		2.10		-	1.20	
	Type IV	50,000	3.8	0.1	97		2.43		-	1.58	
RCD-Isomax	Kuwait	50,000	3.92	1.0	74	28.1	1.69		1.30	1.41	6, 7, 4, 8, 9
		50,000	4.1	0.3	93	41.5	2.49		1.73[a]	1.91	
	Direct I	40,000	3.9	1.0	74	21.80	1.63		0.71[a]	1.15	
	Direct II	40,000	3.9	0.5	87	29.32	2.21		0.98	1.59	
	Modified Direct III	40,000	3.9	0.32	92	35.31	2.65		1.10	1.78	
Residue Desulf. Bp process		50,000	4.0	1.0	75		1.36		1.49	-	10, 11
			4.0	0.5	88		1.57		1.95	-	
			4.0	0.3	93		-		2.47	-	
Resid Hydro-processing Standard Oil Co.	Kuwait	20,000-40,000	4.02	1.0	75	28.6-31.6	2.14 2.37			1.08	12, 13
Go-fining	Arab heavy	18,000-95,000	2.96	0.1	97	$80-150/bpsd capacity				-	14, 15, 4, 16
	Athabasca tar sand		3.97	0.11	97					-	
Resid-fining	Gach Saran	55,000 (Avg.)	2.5	0.3	88	$300-750/bpsd capacity				-	15, 4, 14
	Arab Heavy		4.19	0.3	93					-	
Residue HDS	Kuwait	45,000	4.1	0.95	77		1.38			0.90	17

[a] Major difference in operating cost is price of hydrogen 60¢/MSCF versus 25¢/MSCF.

Table D-3 (continued). ECONOMICS FOR OTHER RESIDUAL OIL UTILIZATION TECHNIQUES

Process	Feed type	Cost basis, bpsd	% S feed	% S product	% S removal	Investment		Operating cost		GCA estimated operating cost, $/bbl	References
						Total MM	Per bbl, capacity, $	Total MM	Per bbl, capacity, $		
HDS-Trickle flow		13,000 (Avg.)	1.33	0.16	88					-	18
IFP Resid and VGO HDS		40,000	2.5	0.3	88		2.01		0.99	1.28	4
Resid ultra-fining	Khafyi	40,000	4.47	1.0	78	26.8	2.01		1.16	1.60	19, 4
Amoco	W. Texas Sour	40,000	3.85	1.0	74	19.8	1.49		0.84	1.17	
	W. Texas Sour		3.85	0.3	92	26.8	2.01		1.17	1.63	
Shell Gasification process		10,000 conversion of vacuum Resid at $2/bbl	5.0			24.4		$0.79/MM Btu of gas or $3.57/bbl		- -	20, 21
Delayed coking VGO/VRDS Isomax		No economic data									22, 23, 24, 25, 9
Flexicoking		20,000	3.43	0.2 equiv.	94% equiv.	17.9	2.73	1.51	0.24	-	26, 27, 4, 28
		20,000	3.66	0.2 equiv.	95% equiv.	20.4	3.09	2.22	0.34	-	
		20,000	4.6	0.2 equiv.	96% equiv.	23.7	3.60	3.23	0.48	-	
Demetalization/ Desulfurization	Venezuelan metals crude	25,000	5.6	1.27	77	23.9	2.89		1.17	1.32	29
	Venezuelan metals atm resid	25,000	2.8	0.64	77	25.2	3.05		0.95	1.11	
L.C. Fining	Kuwait atm resid	40,000	4.05	1.0	75	33.4	2.53			1.21	30, 4, 31
			4.05	0.5	88	34.3	2.60			1.35	
	Gach Saran		2.6	1.0	62	29.8	2.26			1.04	
			2.6	0.5	81	38.9	2.95			1.28	

Table D-4. COMPARATIVE CAPITAL COSTS OF THE CAFB, HDS AND FGD PROCESSES[32]

	CAFB 250 MW,[f] 20% A/F	Grass roots HDS unit with H_2 production (9000 bbl/d unit) (supply for 225 MW)	Grass roots HDS unit with H_2 production (45,000 bbl/d unit) (supply for 1125 MW)	Limestone scrubbing 200 MW unit	Limestone scrubbing 500 MW unit
Process equipment in place		$ 7,761,000[a]	$21,492,000[a]	$3,254,000[a]	$ 6,350,000[a]
Process materials and labor		10,439,000[a]	28,908,000[a]	4,377,000[a]	8,542,000[a]
Total directs		$18,200,000	$50,400,000	7,631,000	$14,892,000
Distributables		2,750,000	7,600,000	1,153,000[b]	2,250,000
Subtotal		$20,950,000	$58,000,000	$8,784,000	$17,142,000
Indirect costs		2,480,000	6,867,000	1,040,000[b]	2,029,000
Total bare cost		$23,430,000	$64,867,000	$9,824,000	$19,171,000
Contingency		1,820,000	5,040,000	763,000	1,489,000
Fee		910,000	2,520,000	382,000	745,000
Total process investment		$26,160,000	$72,427,000	$10,969,000	$21,405,000
New I.D. fan[c]					
Burner costs[d]		200,000 (cat.)	2,000,000 (cat.)		
Total investment		$26,360,000	$72,427,000	$10,969,000	$21,405,000
Start-up costs		1,054,000[e]	2,977,000[e]	878,000	1,712,000
Interest during construction		2,109,000	5,954,000	878,000	1,712,000
Ideal capital costs	$23,975,905	$29,523,000	$83,358,000	$12,725,000	$24,829,000
$/kW	96	131	74	64	50

[a] Proportioned from total directs for CAFB 20% A/F 200 MW unit.

[b] Adjust to CAFB/SWEC %.

[c] Allowance.

[d] SWEC allowance.

[e] Half normal charge due to advanced stage of HDS development.

[f] From reference 34.

Table D-5. COMPARATIVE OPERATING COSTS FOR THE CAFB, HDS AND FGD PROCESSES, \$/yr[a,32]

	CAFB 250 MW, 20% A/F	Grass roots HDS unit with H_2 production (9000 bbl/d unit) (supply for 225 MW)	Grass roots HDS unit with H_2 production (45,000 bbl/d unit) (supply for 1125 MW)	Limestone scrubbing 200 MW unit	Limestone scrubbing 500 MW unit
Limestone or catalyst	\$ 250,000	\$ 356,400	\$1,782,000	\$ 200,000	\$ 500,000
Labor and supervision to operate	149,800	149,800	149,800	210,200	210,200
Steam	Neg.	38,500	192,300	138,000	345,000
Water	Neg.	12,800	64,200	8,000	20,000
Power	722,833	311,800	1,559,200	315,000	787,400
Maintenance	809,400	728,000	2,016,000	610,500	1,191,400
Labor costs	27,000	45,600	45,600	45,600	45,600
Capital charges	3,572,410	4,398,900	12,420,300	1,896,000	3,699,500
Plant overhead	403,716	257,300	805,400	265,500	519,900
Labor overhead	15,000	15,000	15,000	21,000	21,000
Total	\$5,950,149	\$6,314,100	19,049,800	\$3,709,800	\$7,340,000
H_2SO_4 or sulfur credit		(280,700)	(1,403,300)		
Fuel for process heat		1,739,600	8,698,200		
Net		\$7,773,000	\$26,344,760		
Mills/kWh	3.40	4.36	2.96	2.65	2.10
¢/10^6 Btu	34.0	43.6	29.6	26.5	21.0

[a] Basis: 7000 hr/yr, 2.5% S oil, \$4/ton stone, 70¢/1000 lb STM, 1¢/kWh, 8¢/1000 gal. H_2O, 14.9%/yr capital charges, \$1.85/liter for catalyst, \$6/ton of H_2SO_4, Oil and \$1.53/MM Btu for reheat, maintenance, at 8%/yr limes, 4%/yr CAFB, CAT-Ox and HDS as % of total direct investment, labor at \$8/man-hour, plant overhead at 20% of O & M costs, labor overhead at 10% of direct labor costs.

Operating costs for a 250 MW CAFB unit can be extrapolated from Westinghouse's data. The operating costs for HDS, FGD and CAFB are given in Table D-5. The predicted operating costs for FGD are less than either the CAFB and HDS.

It would appear from these most up-to-date predictions that the CAFB process is not cost competitive with the limestone scrubbing FGD process. However, it should be noted that the costs presented in Tables D-4 and D-5 are projections and should be viewed skeptically. Indeed, projections from an earlier Westinghouse report[34] presented in Table D-6 show that FGD should be twice as expensive as the CAFB process.

There are, at present, no actual cost figures available for FGD using limestone scrubbers on oil-fired boilers. The only economic data available for oil-fired boilers using FGD is for the Boston Edison plant with a magnesia scrubber. The results show that in order for this system to be economically competitive, a $3/bbl difference must exist between the cost of high sulfur and low sulfur fuel oil.[32] Since low sulfur oil can be prepared from high sulfur feedstock by HDS for under $3/bbl, it appears that FGD using a magnesia scrubber is a costly way of meeting air pollution standards for SO_2 emissions.

This may also be true for FGD using limestone scrubbing when actual cost figures for FGD on oil-fired boilers or for the CAFB are evaluated.

Table D-6. 1972 PROJECTED COSTS FOR THE CAFB AND FGD PROCESSES, ¢/10^6 Btu, 370,000 lb steam/hr, new installation[34]

	Capital charges	Desulfurization cost	Labor	Sorbent	Power	Solids disposal	Total
Low sulfur oil	4.58	26.0	5.2	-	0.7	-	36.48
CAFB	13.92		11.7	2.6	1.3	1.6	31.12
Conventional with wet scrubbing	28.02		11.7	4.5	1.3	17.5	63.02

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